Study of Drag Reduction by Zwitterionic and Non-Ionic Surfactants in Low Temperature Ethylene Glycol/Water Recirculation Systems

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Introduction

District cooling systems are an efficient way to remove heat from buildings and are being utilized around the world. Although they typically use water chilled at a central station to 5˚C as the cooling fluid, adding ethylene glycol to the water allows the fluid to be chilled to –5˚C, which will increase the cooling capacity per unit mass of fluid circulated and reduce the amount of cooling fluid required, and reduces pumping energy requirements significantly.

Drag reduction is a flow phenomenon in which a reduction in turbulent friction occurs. Drag reduction can be induced by polymers, fibers, soaps, or surfactants in solution. A surfactant is a molecule consisting of a hydrophilic polar head group and a hydrophobic end typically with a long carbon chain. Surfactants were chosen for this project and are appropriate for recirculation systems due to their ability to reassemble into micelles quickly after being degraded by mechanical stress such as in a pump. Introducing surfactants into polar solvents such as 20% ethylene glycol/water causes interactions between the surfactant and solvent. The hydrophobic tail of the surfactant repulses the solvent, and forms micelles in order to effectively avoid contact with the solvent. Micelles take three general forms: spheres, elongated cylinders known as threads, or vesicles. It should be noted that threadlike micelles are generally accepted to be necessary for drag reducing behavior to occur. Therefore, through the addition of surfactants into the ethylene glycol/water systems, the drag can be reduced in the turbulent flow through the pipes due to micelle formation, thus reducing the pumping energy required to circulate the fluid and saving energy and money.

There are generally four types of surfactants: cationic, anionic, non-ionic, and zwitterionic. Cationic surfactants are positively charged and typically are effective drag reducers, but are not very biodegradable. Anionic surfactants are negatively charged, which allows them to interact with any positive ions present in solution (such as calcium and magnesium ions in tap water). Non-ionic surfactants do not have a net charge, and are typically biodegradable. Zwitterionic surfactants also do not have a net charge, but they are different in that they have a positive and negative charge both present on the molecule in different regions. This research focused on testing zwitterionic, zwitterionic/anionic, and non-ionic surfactants, which are more biodegradable and therefore environmentally benign. Both commercial surfactants and surfactants synthesized by Dr. Hart and post-doc Dr. Oba, organic chemists in the Department of Chemistry, were tested.

The purpose of this project was to determine an effective formulation for both zwitterionic and non-ionic surfactants in 20% (by weight) ethylene glycol/water that could be used in district cooling systems for the temperature range of -5 to 15 °C. Drag reduction in other solvents such as water, 30% (by weight) glycerol/water, and 25% propylene glycol/water were studied as well. One intention of this project was to find more environmentally benign surfactants with drag reducing ability equal to that of cationic surfactants. Additions of sodium nitrite have been shown to contribute to drag reduction as well as being an effective means of preventing corrosion in the metal pipes of a circulation system when used in combination with zwitterionic, non-ionic, or zwitterionic/anionic surfactant solutions. Finding an effective concentration of sodium nitrite to add to surfactant solutions was one goal of this project. In some cases, additions of anionic surfactants to zwitterionic surfactants has enhanced effectiveness in reducing drag, and therefore determining an effective zwitterionic:anionic ratio was another goal of this project. Overall, finding an effective drag reducing system by evaluating formulations was the objective of this project.

Literature Review

A) Surfactants

Surfactants, or surface-active agents, are characterized by the coexistence of a hydrophobic tail and hydrophilic head group in one molecule, making them amphiphilic compounds. This structure can be seen in Figure 1.

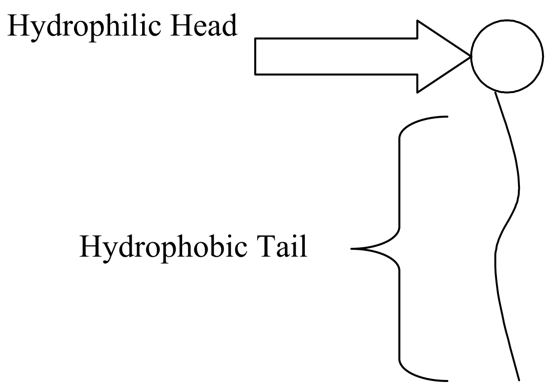


Figure 1: Surfactant Structure Diagram

The hydrophobic tail is typically a long alkyl chain and the hydrophilic head is ionizable, polar, polarizable, or suitable for forming hydrogen bridges (8). In a polar solvent, the hydrophobic groups cluster together, leaving the polar groups to surround them and contact the solvent. In a non-polar solvent, the hydrophilic groups cluster together while the hydrophobic groups are exposed to the solvent. These structures are held together by hydrophobic interactions, while if head groups are charged, electrostatic interactions play a role (1). Steric factors also have significant effects on micelle structures.

B) Micelles

The self-associating interactions of surfactant molecules in polar solvents cause formation of assemblies called micelles in which the non-polar portions concentrate in the center while the polar ends lie on the surface in contact with the polar solvent. The size of these aggregates depends on the nature of the surfactant molecule and varies with the surfactant concentration and with the temperature. It depends also on the nature and concentration of added salt. The bonds between surfactant aggregates are weak, and the micelles continuously exchange molecules with the solvent, break, and reassemble (5).

Micellization is a feature of surfactant solutions above their critical micelle concentration (CMC). Two CMC levels exist, with different shaped micelles formed at each successive concentration. At CMC, spherical micelles are formed. Changes in temperature have little effect on the CMC. At a higher critical micelle concentration, CMC_{II}, thread-like micelles are formed. As temperature is increased, CMC_{II} increases. The length of thread-like micelles has been shown to increase with increase in surfactant concentration and decrease in temperature (7). Micelle aggregation number also increases rapidly with increase of hydrocarbon chain length and decreases with increasing cross-sectional area of the head group (9). Figures 2 and 3 show what the spherical and thread-like micelle structures look like above their respective critical micelle concentrations.

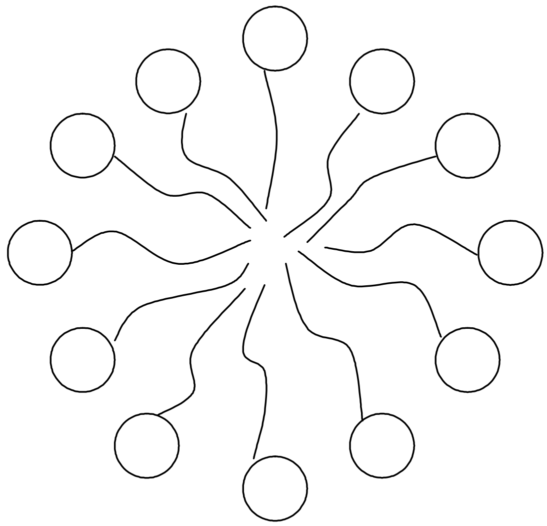


Figure 2: Spherical Micelle Diagram

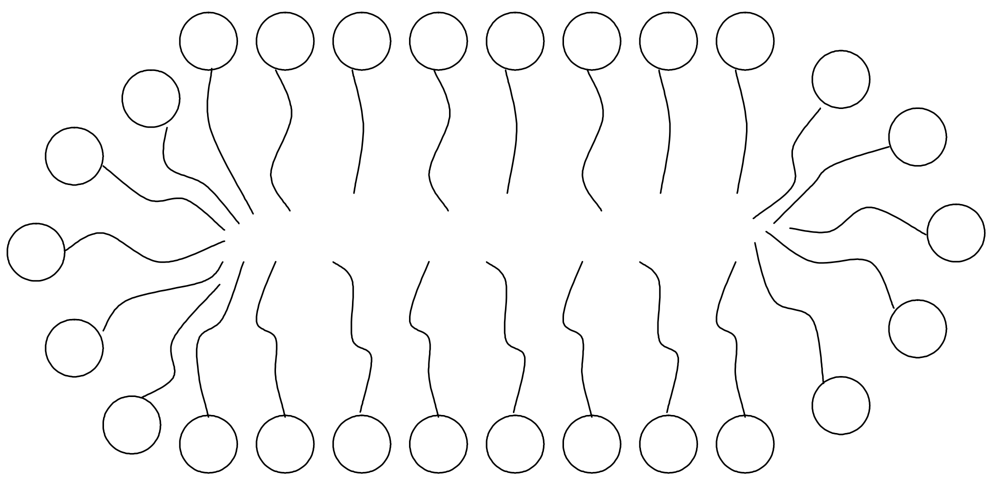


Figure 3: Thread-Like Micelle Diagram

C) Drag Reduction

Drag reduction by additives is a phenomenon that reduces the drag (friction coefficient) in turbulent flow. The most efficient types of additives are high molecular weight polymers. They are, however, not suitable for recirculation systems, as the polymer chains break when exposed to high shear stresses in the flow, such as in passing through a pump, losing their original high molecular weight. Surfactants have lower molecular weight and form micellar aggregates if a required minimum concentration of surfactant is exceeded, thus causing drag reduction. New polymer additive must then be added to maintain drag reduction. In surfactants, the mechanical degradation is only temporary as the micelles can reassemble after mechanical degradation and so are suitable for recirculation systems (2).

1) Zwitterionic Surfactants

Zwitterionics are a special kind of non-ionic surfactant in that they have both positive and negative charges on the surfactant molecule, and hence no net charge (9). Unique properties of zwitterionic surfactants include tolerance to hard water, strong electrolytes, and oxidizing and reducing agents, low toxicity, and compatibility with all other types of surfactants. These surfactants are currently being used in shampoos and as latex stabilizers (3).

2) Non-Ionic Surfactants

Non-ionic surfactants don't have any charges and are less affected by ions. In solutions containing non-ionic surfactants, the temperature at which the maximum drag reducing ability is observed is close to the cloud point, or coacervation temperature, of the surfactant solution (9).

3) <u>Zwitterionic/Anionic Surfactant Combinations</u>

It has been found that improvements in drag reduction are achieved by the use of a betaine (zwitterionic) surfactant in combination with an anionic surfactant. Both the betaine surfactant and the anionic surfactant are readily biodegradable and the combination gives an excellent drag reducing effect within a wide temperature range. Solutions of the betaine and anionic surfactants are especially suited for use in water-based systems flowing in long conduits, such as circulation systems for district heating and cooling systems (4).

4) <u>Sodium Nitrite</u>

Sodium nitrite is a salt and is a corrosion inhibitor. It also has significant effects on the drag reducing effectiveness of some surfactant solutions. In such cases it plays an important role in affecting micellar growth. This is especially true in zwitterionic surfactants. In solutions containing these surfactants, salts have the ability to neutralize these charges and cause more micellar growth (9). In general, the presence of different ions in water in the form of low concentrations of salts decreases the shear or apparent viscosity of a drag reducing surfactant solution as compared to a distilled water solution of the surfactant (8).

D) Fluid Flow Concepts in Drag Reduction

A fluid is classified by the manner in which its viscosity changes with shear rate. Newtonian fluids follow Newton's law of viscosity, which is typical for small molecules such as water. The viscosity of the fluid is independent of the shear rate, as shown in equation (1).

$$\tau = \mu * \frac{du}{dy} \tag{1}$$

In a non-Newtonian fluid, the viscosity is often a strong function of shear rate. This is referred to as an apparent viscosity and is defined in equation (2):

$$\tau = \mu_{app} * \frac{du}{dy} \tag{2}$$

Surfactant solutions with drag reducing ability have apparent viscosities that decrease as shear rate is increased. These are called shear thinning fluids, and many equations can be used to fit the apparent viscosity as a function of shear rate.

In pipe flow, shear stresses are highest at the wall. The main drag reduction equation is equation (3):

$$\%DR = \frac{f_s - f}{f_s} * 100 \tag{3}$$

In this equation, f_s is the friction factor of the pure solvent and f is the friction factor of the solution containing the drag reducing surfactant in that solvent. The friction factor of the solution with surfactant is determined using equation (4).

$$f = \frac{D * \Delta P_{corr}}{2 * L * \rho * v^2} \tag{4}$$

ΔP_{corr} is the corrected pressure drop, L is the length of the test section, and v is the velocity obtained from flow rate measurements and the cross sectional area of the tube (4).The friction factor of the solvent can be accurately estimated from the von Karman equation.

$$\sqrt{\frac{1}{f_s}} = 4.0 * \log(\mathrm{Re}^* \sqrt{f_s}) - 0.4 \tag{5}$$

The Reynolds number in this equation (Re) is defined as:

$$\mathrm{Re} = \frac{\rho v D}{\mu} \tag{6}$$

In equation (6), ρ is the density, v is the fluid velocity, D is the inner diameter of the pipe, and μ is the solvent viscosity.

Experimental Procedures

A) Surfactants and Additives

The surfactants tested are listed in Table 1. The table gives the classification of each surfactant, the additives used in conjunction with the respective surfactant, the solutions in which the surfactants were tested, and source of the surfactant.

Table 1: Surfactants Tested

Surfactant	Classification	Solutions	Additives	Source
Oleyl Trimethylaminimide	Zwitterionic	Water	Sodium Nitrite	Dr. David J. Hart
		20% Ethylene Glycol/Water		
DR0206	Zwitterionic / Anionic Mixture	Water	Sodium Nitrite	Akzo Nobel
		20% Ethylene Glycol/Water		
SPE98300	Zwitterionic / Anionic Mixture	Water	Trilon A	Akzo Nobel
		20% Ethylene Glycol/Water	Formaldehyde	
		30% Glycerol/Water	Sodium Nitrite	
Beraid DR DC 620	Non-Ionic	Water	Sodium Nitrite	Akzo Nobel
		20% Ethylene Glycol/Water		
		30% Glycerol/Water		
		25% Propylene Glycol/Water		
Chemoxide OL	Zwitterionic	20% Ethylene Glycol/Water	Sodium Nitrite	Chemron
		30% Glycerol/Water		
Oleyl Betaine	Zwitterionic	Water	Sodium Dodecyl Sulfate (SDS, an anionic surfactant)	Dr. David J. Hart
		20% Ethylene Glycol/Water	Sodium Dodecyl Benzenesulfonate (SDBS, an anionic surfactant)	
			Sodium Nitrite	
Oleyl (Chem)Betaine	Zwitterionic	Water	Sodium Dodecyl Benzenesulfonate (SDBS, an anionic surfactant)	Chemron
		20% Ethylene Glycol/Water	Sodium Nitrite	
N-7	Non-Ionic	Water	Sodium Nitrite	Dr. David J. Hart
N-13	Non-Ionic	20% Ethylene Glycol/Water	Sodium Nitrite	Dr. David J. Hart

Table 2 lists the surfactants tested and the chemical structure of each surfactant.

Table 2: Surfactant Structures

Surfactant	Components/Structures
Oleyl Trimethylaminimide	$CH_3(CH_2)_7CH=CH(CH_2)_7CON^-N^+(CH_3)_3$
DR0206	20% (10%-30%) Myristylamidopropylbetaine; $CH_3(CH_2)_{12}CONH(CH_2)_3N^+(CH_3)_2$-$CH_2COO^-$
	10% (5-15%) Rapeseedamidopropylbetaine; $CH_3(CH_2)_7CH=CH(CH_2)_{11}CONH(CH_2)_3N^+(CH_3)_2CH_2COO^-$
	5% (1%-10%) C_{10}-C_{13} Alkylbenzene sulphonic acid, sodium salt
	30% (25%-35%) 2-propanol; $CH_3CH(OH)CH_3$
	30% (25%-35%) Water; H_20
SPE98300	27% (10%-30%) C_{16}-C_{18} Alkylbetaine; R-N^+ $(CH_3)_2(CH_2)COO^-$
	6.7% (5%-10%) C_{10}-C_{13} Alkylbenzene sulphonate; R-(C_6H_4)-SO_4^-
	30% Isopropanol ; $CH_3CH(OH)CH_3$
	33% Water; H_2O
Beraid DR DC 620	50% (30%-60%) C_{16}-C_{18} (unsaturated) Alcohol ethoxylate (unsaturated); R-$(OCH_2CH_2)_n$-OH
	50% (30%-60%) C_{12}-C_{18} and C_{18} (unsaturated) Alkyl monoethanolamide ethoxylate; R-$CON(CH_2CH_2OH)$-$(OCH_2CH_2)_n$-OH
Chemoxide OL	$CH_3(CH_2)_7CH=CH(CH_2)_8N^+(CH_3)_2O^-$
Oleyl Betaine	$CH_3(CH_2)_7CH=CH(CH_2)_7N^+(CH_3)_2CH(CH_3)COO^-$
Oleyl (Chem)Betaine	$CH_3(CH_2)_7CH=CH(CH_2)_7N^+(CH_3)_2CH(CH_3)COO^-$
N-7	$CH_3(CH_2)_7CH=CH(CH_2)_7CONH(CH_2CH_2O)_7$-$CH_3$
N-13	$CH_3(CH_2)_7CH=CH(CH_2)_7CONH(CH_2CH_2O)_{13}$-$CH_3$

B) Drag Reduction Experiments

1) Preparation of Surfactant Solutions

Surfactants and additives were weighed out in beakers or weighing dishes. 21-L solutions were measured volumetrically in 4-L beakers. The components of each solution were combined in a 30-L polyethylene-lined container, where they were mixed for eight hours by an electric mixer. The solution was then equilibrated for a minimum of 24 hours, after which it was tested in the recirculation system.

2) Operating Procedure

A flow sheet of the recirculation system is given in Figure 4, with arrows showing the path of the fluid through the system.

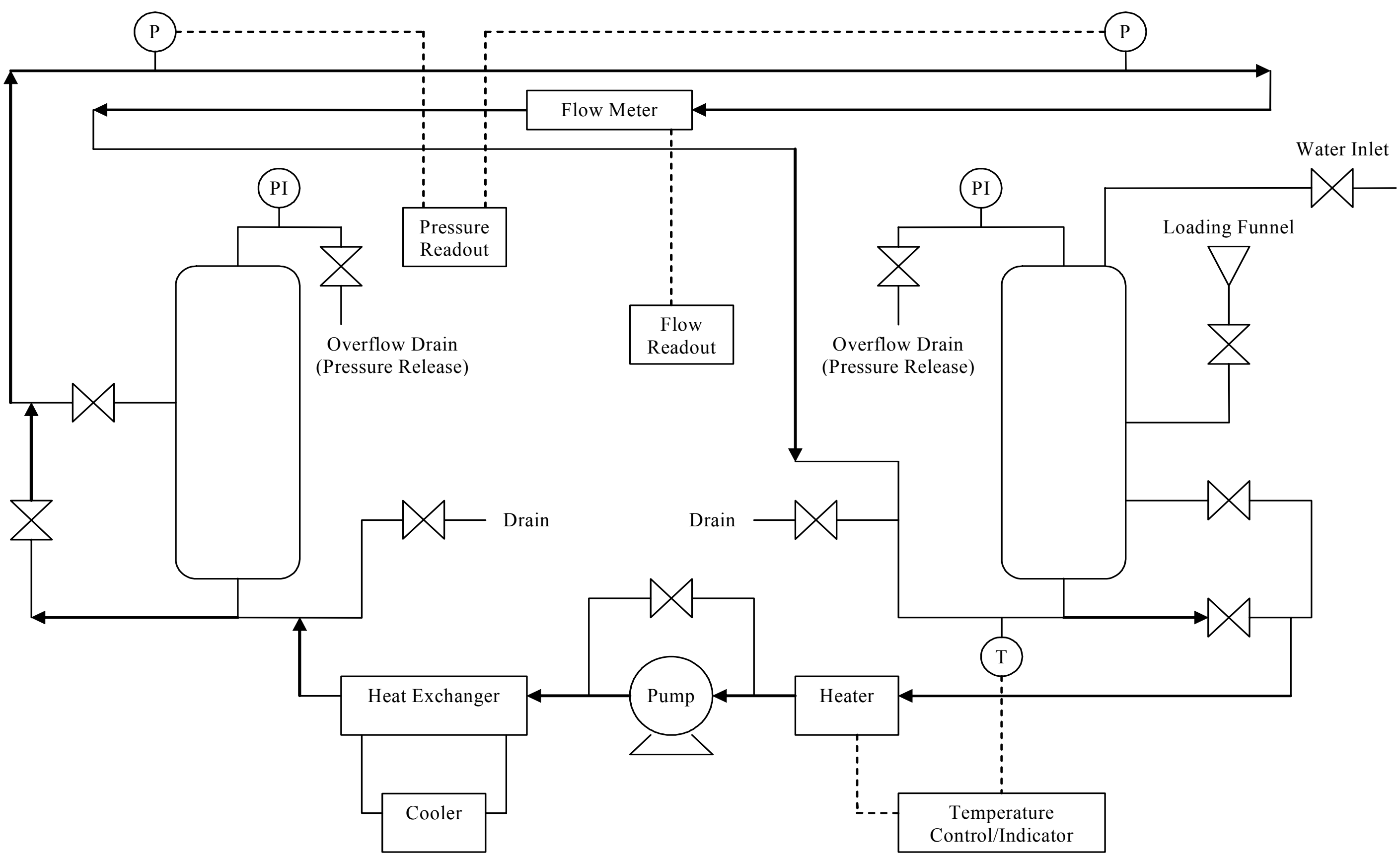


Figure 4: Flow Sheet of the Recirculation System

The temperature in the system could be controlled from -5 °C to 90 °C. The pressure drop was measured by pressure transducers across a specified length of pipe. A magnetic flow meter measured the flow rate of the solution through this length of pipe. The 21-L prepared solutions were introduced into the system through a loading funnel near the top of the right tank. The solutions were circulated through the system by turning on the pump. The temperature was set to the desired level, and the system was allowed to equilibrate at this temperature for approximately 5 minutes. The pump was then shut off, and an initial pressure reading (ΔP_0) was taken when the flow meter was at 0.00 GPM. The pump was then turned back on, and the temperature was once again allowed to equilibrate. The pump speed was then slowly increased, with flow rate and pressure drop measurements taken at each successive flow rate. Approximately ten flow rate and pressure drop readings were taken at each temperature. The temperature fluctuated by ± 0.5 °C of the desired temperature during these measurements.

Once all temperatures had been tested, the solution was drained through the drain pipes at the bottom of the system. To clean the recirculation system, it was initially filled with tap water and drained. This was done two times, and after filling the system with tap water a third time, the pump was turned on and the heater was set to 60 °C. Water was circulated at this temperature for a minimum of 20 minutes, and the water was then drained. The system was then filled and drained once more with cold tap water.

3) Equipment in the Recirculation System

A photograph of the recirculation system can be seen in Figure 5.

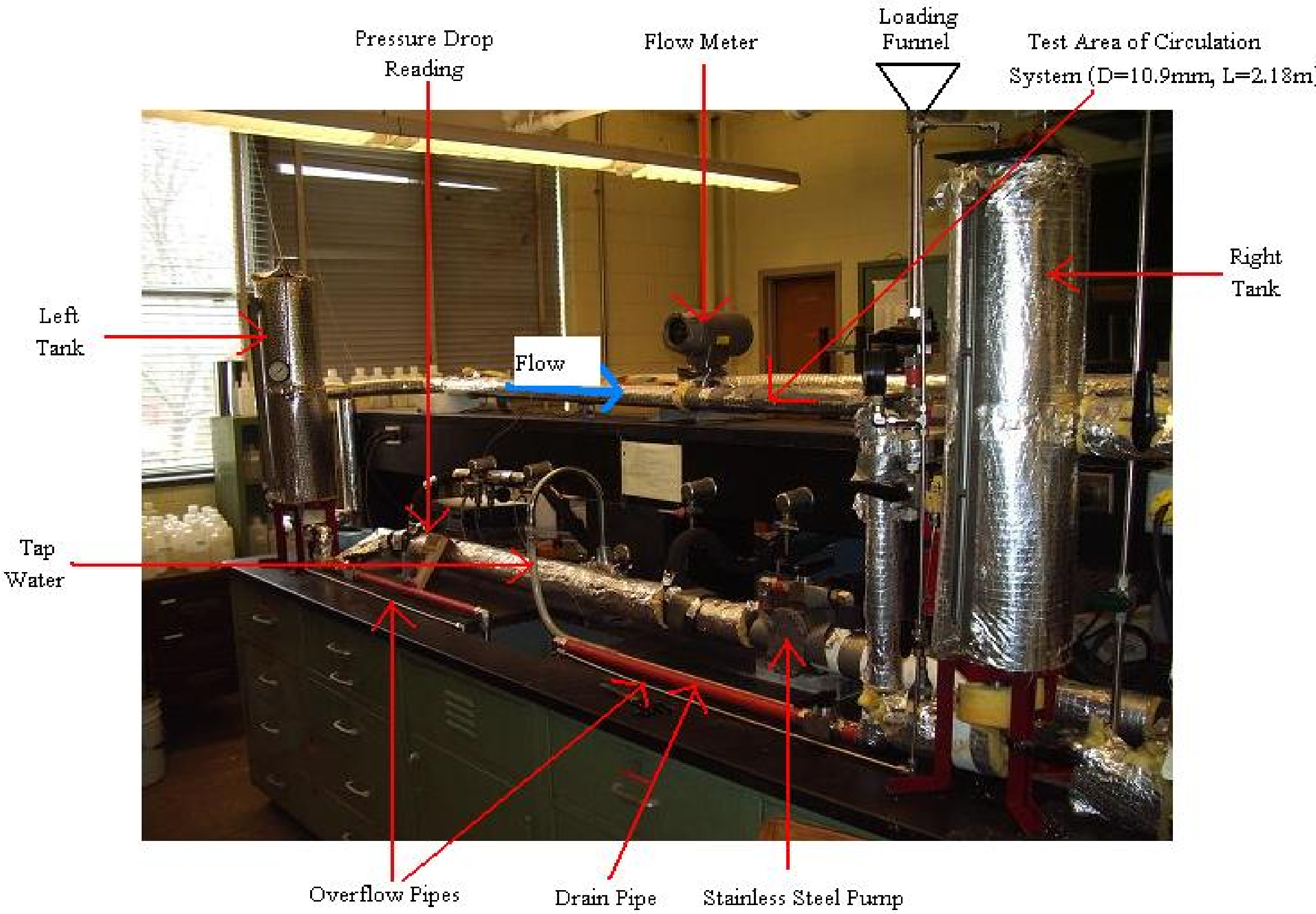


Figure 5: Photograph of the Recirculation System

The recirculation system consisted of two 4-gallon stainless steel surge tanks, which dampened pressure fluctuations and reduced temperature gradients within the flow system. All pipes and fittings and the pump were stainless steel. All sections of the system were insulated by fiberglass in order to minimize heat transfer to the surroundings. The pressure drop was measured across a 2.18 m long section of the stainless steel pipe with a diameter of 10.9 mm. A Validyne differential pressure transducer (Model DP 15-40; pressure range = 0 ~ 12.5 psi) was used to measure these pressure drops. A stainless steel pump with viton seals and gears, which had a maximum setting of 35 GPM, drove the flow through the system. It was connected to a Dayton

SCR motor controller (Model 4Z377B) that controlled the pumping rate. The flow rates were measured by a calibrated Rosemount Series 8700 magnetic flow meter attached to the pipe near the region of the pressure drop measurement.

The heater was a 2 kW heater connected to a variac, and could be controlled from -10 °C to 90 °C with increments of ±0.1 °C. It supplied heat for runs at temperatures greater than 20 °C, and it was used as the set point for all temperatures. A 750 W trimmer heater connected to a temperature controller in the chiller loop helped steady the temperature of the cooling fluid when it became too low. The cooler was a PolyScience chilling unit (Model KR-60A), which included a ½-hp compressor and a constant temperature circulator. Heat was removed through a stainless steel shell and tube heat exchanger containing coolant (a 1:1 mixture of ethylene glycol and water). The heat exchanger was insulated with polyethylene foam to prevent heat loss to the environment. A thermoregulator was used to control the cooling temperature between -30 and 30 °C, but the lowest temperature attainable in the flow system was approximately –7 °C (6).

4) <u>Calculations from Data</u>

A spreadsheet provided by Ying Zhang performed drag reduction calculations for the data entered into the spreadsheet. The friction factor (f) was calculated from the pressure drop measurement, while the friction factor for the solvent (f_s) was calculated from the solvent Reynolds number. This was used to determine the drag reduction percentage using equation (7).

$$\% \text{ Drag Reduction} = \frac{f_s - f}{f_s} * 100 \tag{7}$$

C) Swirl Decay Times

Swirl decay time is a measurement performed to give a rough estimate of the viscoelasticity of a fluid. A sample of approximately 30-50 mL of solution was obtained or made and placed in a small beaker. A one-inch stir bar is added to this solution, and the beaker is covered with Parafilm and placed on a magnetic stirrer. The stirrer was turned to a setting of 7 and allowed to stir at this setting for 10 seconds, after which it was promptly turned off. A stopwatch was started when the stir bar stopped spinning. The stopwatch was stopped when the fluid began to recoil. This was designated the swirl decay time. Solutions with lower swirl decay times often had higher drag reduction. If a solution did not recoil, it was considered to have an infinite swirl decay time.

Results and Discussion

The results for each surfactant tested will be discussed, but it should be noted that only plots with **significant drag reduction** (**> 50%**) will be included in this section so that data trends can be seen. Plots with insignificant drag reduction can be found in the Appendices.

A) Oleyl Trimethylaminimide

Oleyl Trimethylaminimide is a zwitterionic surfactant synthesized by Dr. Hart and Dr. Oba. Its structure can be seen in Figure 6. This surfactant was tested in water and 20% ethylene glycol/water, with the focus on solutions in 20% ethylene glycol/water.

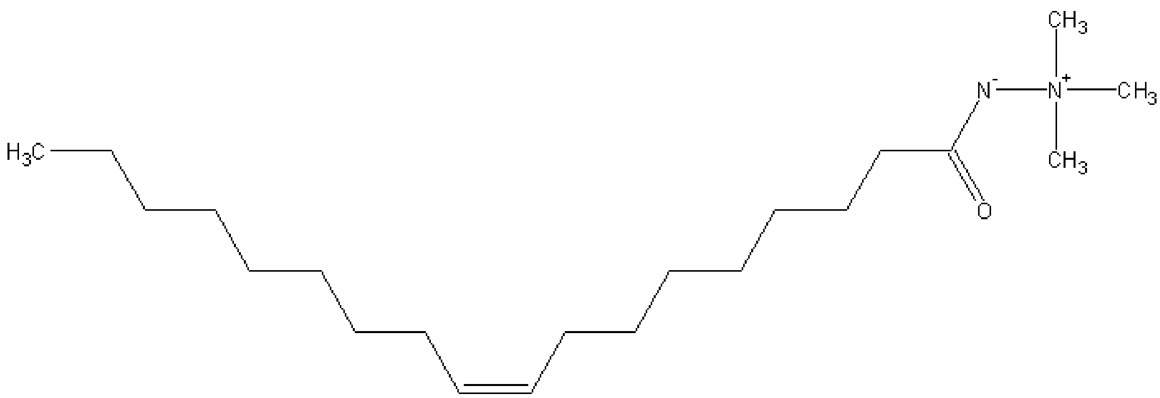


Figure 6: Oleyl Trimethylaminimide Structure

1) Water

An initial solution of oleyl trimethylaminimide (1000 ppm) in water was tested. This solution had good drag reducing behavior in the range of 5 to 30 °C, with the significant drag reducing behavior peaking at low Reynolds numbers at around 50 – 60% drag reduction at low temperatures (5 and 10°C) and 70% drag reduction at higher temperatures (20 and 30 °C). The trends for this solution can be seen in Figure 7.

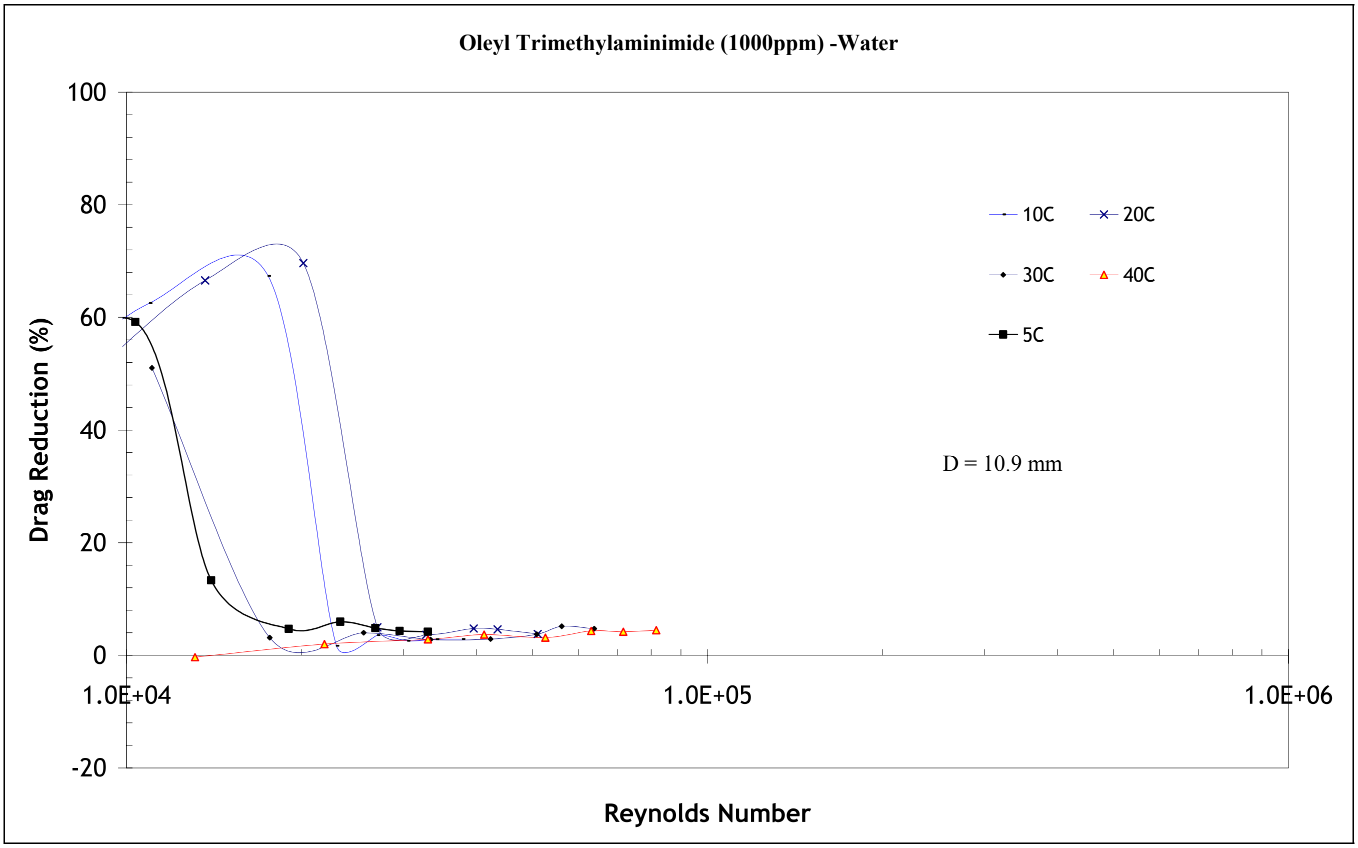


Figure 7: Oleyl Trimethylaminimide (1000 ppm) in Water

2) <u>20% Ethylene Glycol/Water</u>

i) <u>1000ppm</u>

Following the 1000 ppm oleyl trimethylaminimide solution in water tests, the solvent was changed to 20% ethylene glycol/water. The drag reduction results for this solution were significantly better than for the surfactant in water, with the significant drag reducing temperature range moving from 5 – 30°C in water to 0 – 60 °C in 20% ethylene glycol/water. The peaks in this solution were broader and higher at all temperatures, with peaks in the 60 -70% drag reduction range. The trends can be seen in Figure 8. Due to the better performance of oleyl trimethylaminimide in the 20% ethylene glycol/water solvent, further exploration of this surfactant's drag reducing behavior was carried out with this solvent.

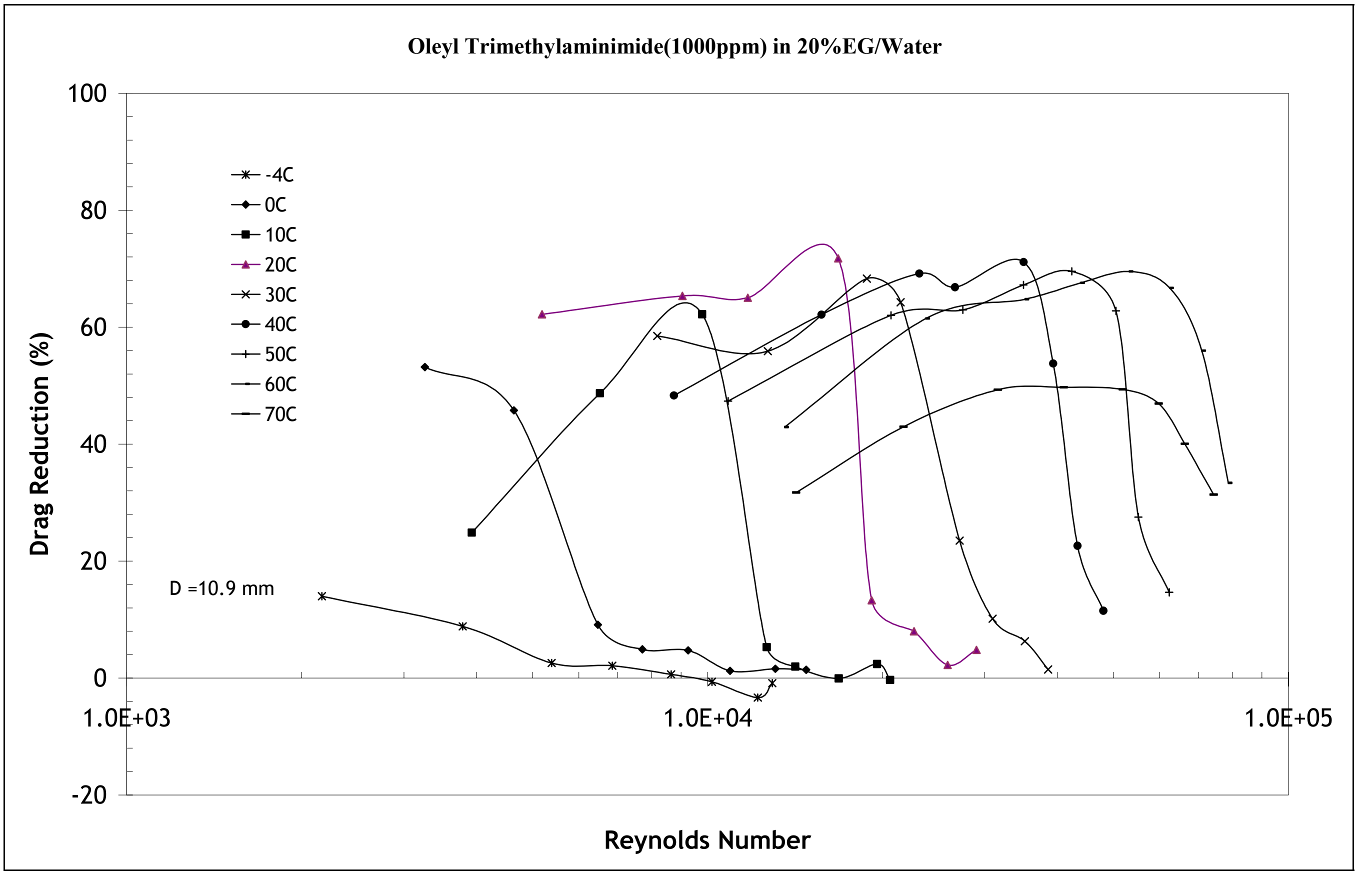


Figure 8: Oleyl Trimethylaminimide (1000 ppm) in 20% Ethylene Glycol/Water

The effect of the addition of sodium nitrite to oleyl trimethylaminimide (1000 ppm) solutions in 20% ethylene glycol/water was pursued next. In the first experiment, 3 mM sodium nitrite was added to the solution and the drag reducing behavior was affected. Significant drag reduction only occurred up to 40 °C instead of 60 °C. Meanwhile, at the lowest temperature (-4°C), the maximum drag reduction increased (from 14 to 23%).

Overall, at lower temperatures the peaks tended to become slightly higher while at higher temperatures they became lower and less broad. The trends can be seen in Figure 9.

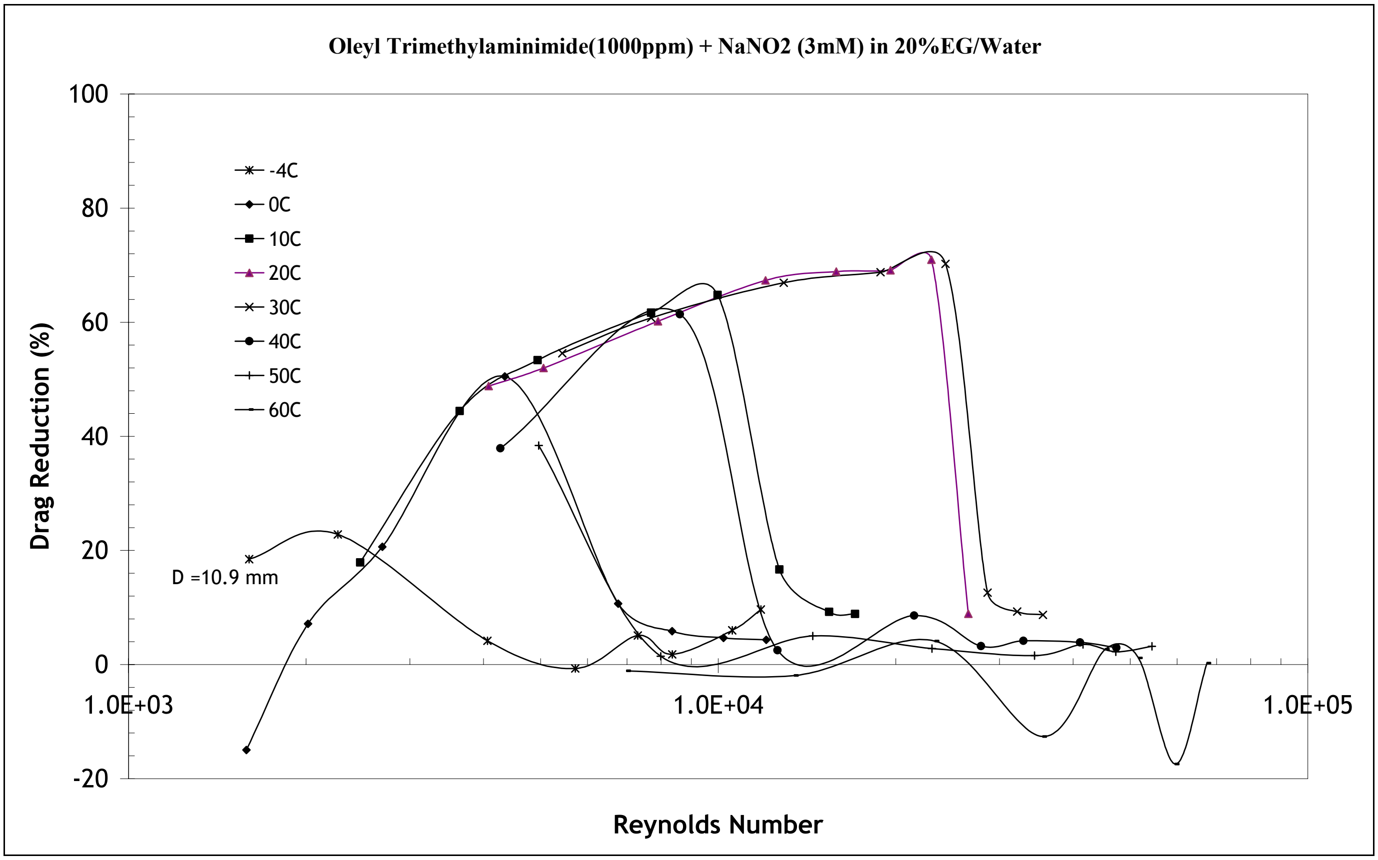


Figure 9: Oleyl Trimethylaminimide (1000 ppm) + NaNO2 (3 mM) in 20% Ethylene Glycol/Water

The solution containing 6 mM sodium nitrite continued the trend of sodium nitrite's effects, with the peak at -4 °C reaching 37%. The significant drag reduction temperature range remained the same at 0 to 40 °C. Overall, the peaks at this sodium nitrite concentration were lower and less broad than the previous two solutions. The trends can be seen in Figure 10.

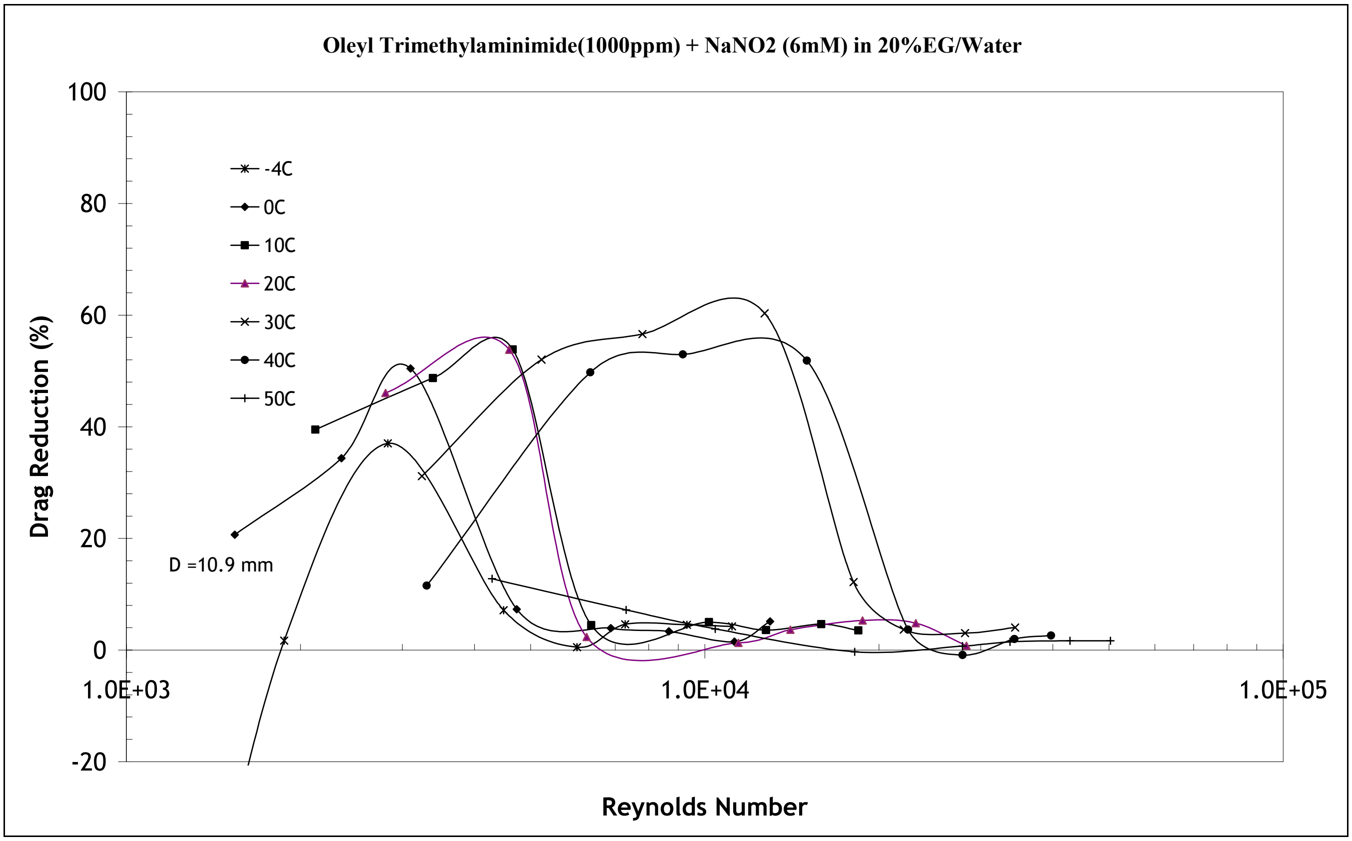


Figure 10: Oleyl Trimethylaminimide (1000 ppm) + NaNO2 (6 mM) in 20% Ethylene Glycol/Water

Experiments with oleyl trimethylaminimide (1000 ppm) with 30 mM of sodium nitrite in 20% ethylene glycol/water were inconsistent. Four experiments involving this solution were performed, and they will be discussed in the order they were performed. The first test's plot can be seen in Figure 11, and the results were very good. It continued the trend observed with 3 and 6 mM sodium nitrite, with low temperature drag reducing behavior improving while the higher temperature behavior became poorer. The significant drag reduction temperature range was reduced to -4 to 30 °C. The major difference with this solution was the noticeably broader peaks, with drop offs at all temperatures at very high Reynolds numbers. Further reduction in drag reduction was observed at 0 °C at which the drag reduction was lower than at -4 °C or at 10 °C. This first solution was tested again to further examine this "gap" phenomenon at 0 °C. The "gap" phenomenon is a strange behavior observed in some surfactant solutions where at one temperature significant drag reduction is observed while at a slightly higher temperature, no drag reduction is observed. At an even higher temperature, significant drag reduction is observed once again. This behavior has not been explained.

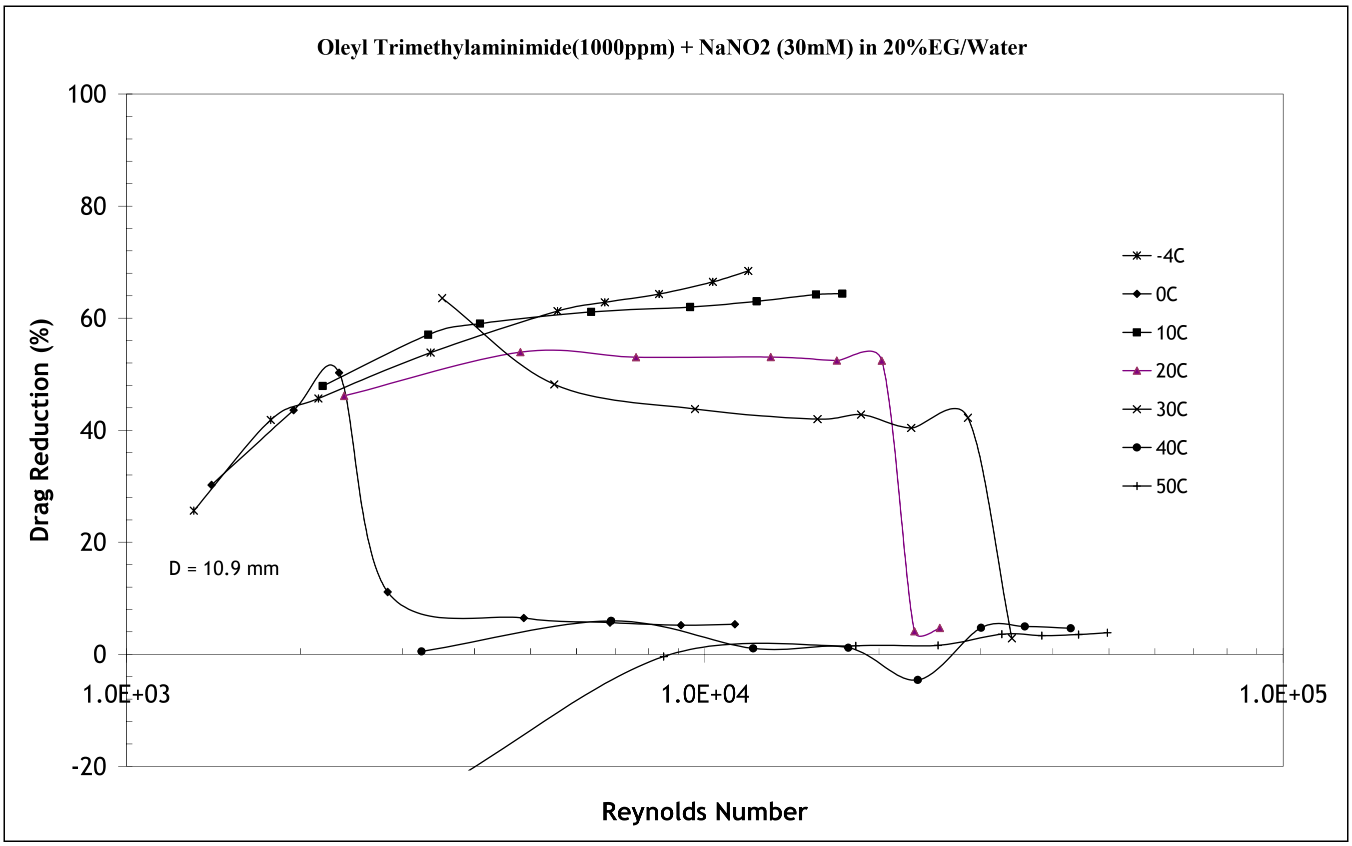


Figure 11: Oleyl Trimethylaminimide (1000 ppm) + NaNO2 (30 mM) in 20% Ethylene Glycol/Water

The second test consisted of the same solution after it had been stored for three days. The drag reduction trends observed for the solution in the second test were more consistent with the trends in the solutions containing 3 and 6 mM of sodium nitrite, that is, they had similar height and broadness of peaks. The significant drag reduction temperatures were -4 and 10 to 20 °C, which coincided with the “gap” phenomenon noticed in the first testing of this solution at 0 °C. The trends can be seen in Figure 12.

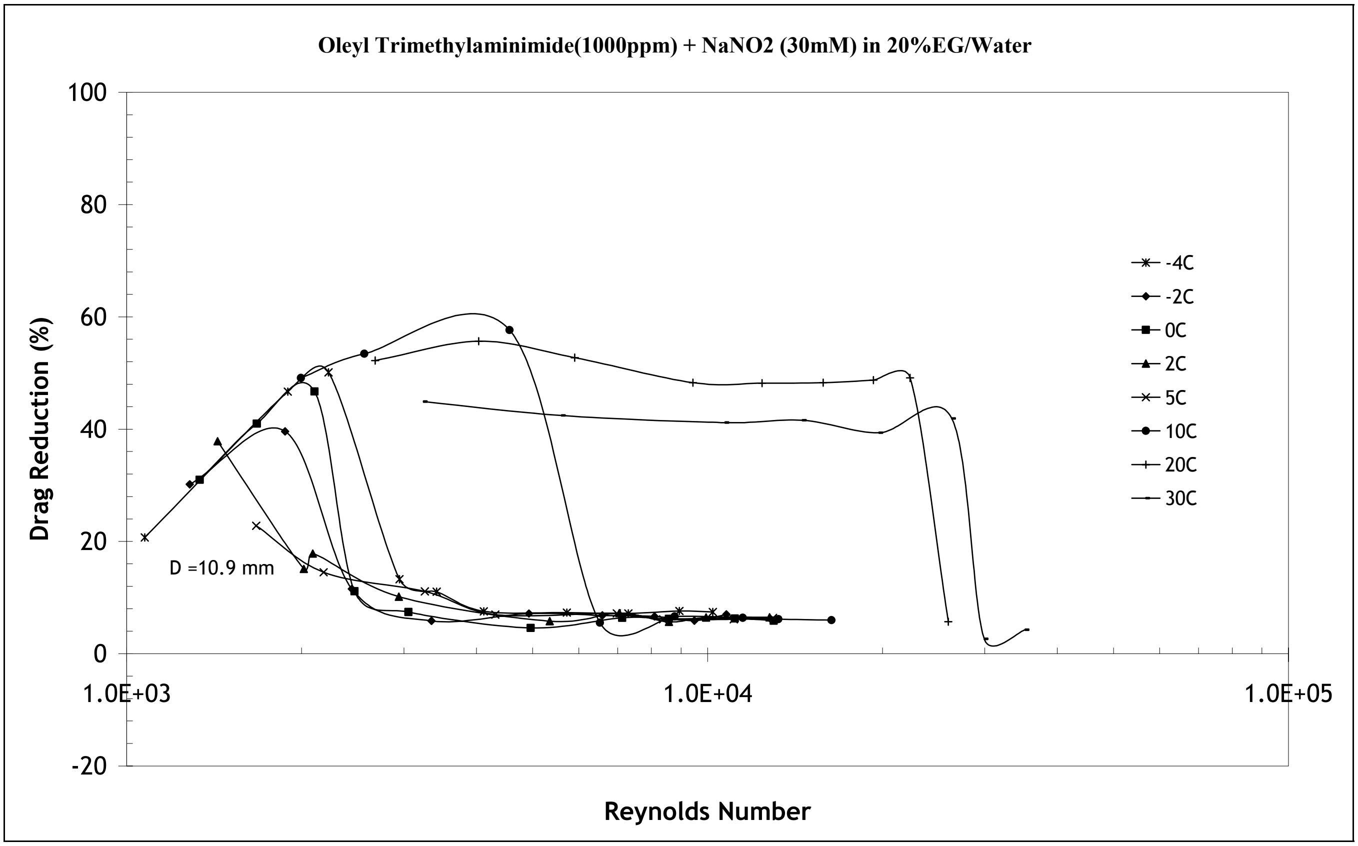


Figure 12: Oleyl Trimethylaminimide (1000 ppm) + NaNO2 (30 mM) in 20% Ethylene Glycol/Water: TEST 2

The difference in behavior of experiments with the same surfactant in solution might be attributed to a change in the solution over time. In order to determine if this was the case, a fresh solution containing a newly synthesized sample of oleyl trimethylaminimide (1000 ppm) and sodium nitrite (30 mM) in 20% ethylene glycol/water was made. The puzzling results can be seen in Figures 13 and 14.

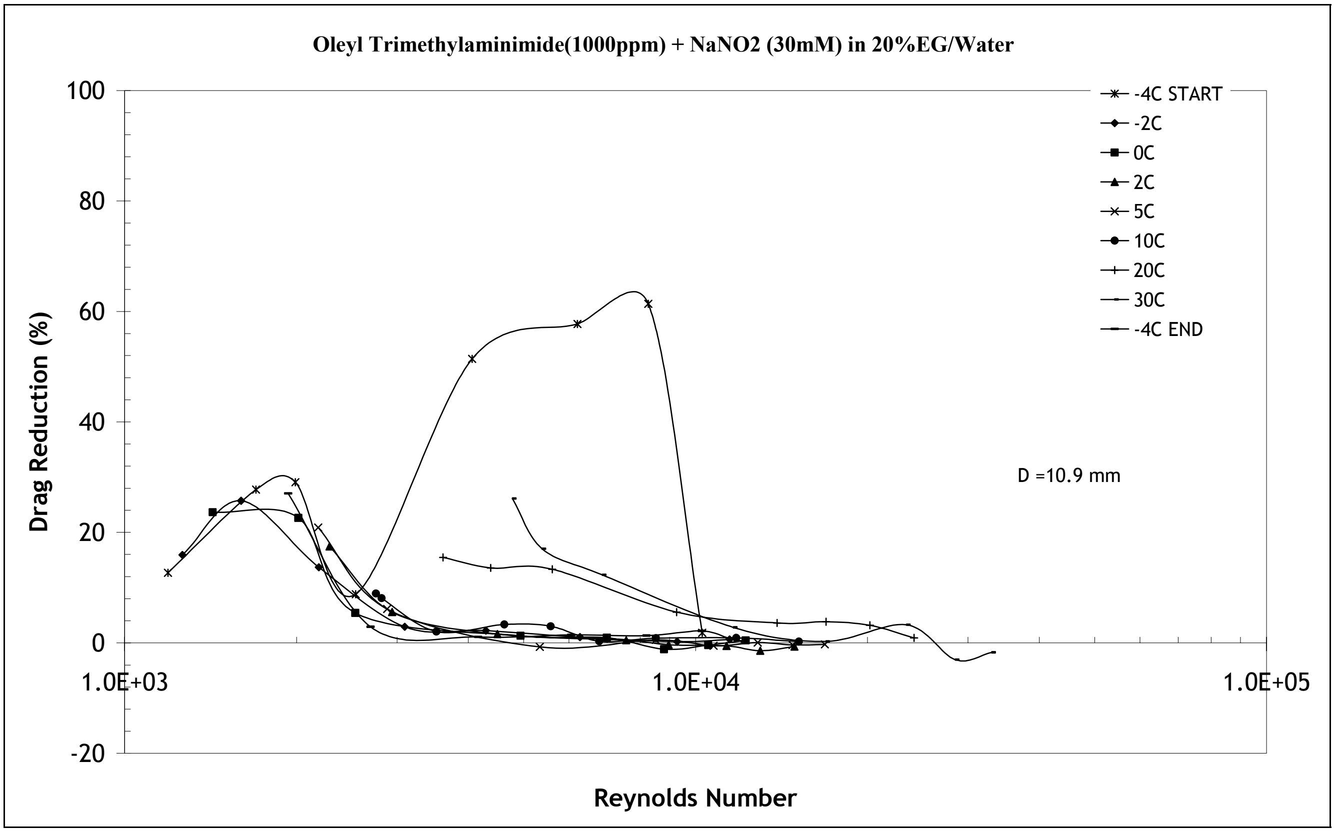


Figure 13: Oleyl Trimethylaminimide (1000 ppm) + NaNO2 (30 mM) in 20% Ethylene Glycol/Water: TEST 3

The first experiment with the new solution gave strong drag reducing behavior at the initial temperature of -4 °C, while at all other temperatures it gave mediocre results, with many of the temperatures exhibiting nearly the same behavior, consisting of an initial small peak and then drop off. Also, at the end of this series of runs to 30 °C, the temperature was brought back down to -4 °C and poorer drag reduction behavior was observed. Another experiment with the new solution gave similar results at many temperatures regarding the small peak and drop off. This time, however, significant drag reduction was observed at 30 °C. These results were mostly inconsistent with each other and with the two previous tests. One possible reason for this strange behavior could be that the surfactant samples were different. However, NMR analyses did not show any differences. Nevertheless, 30 mM of sodium nitrite is not considered a stable additive for this solution, and further testing needs to be done.

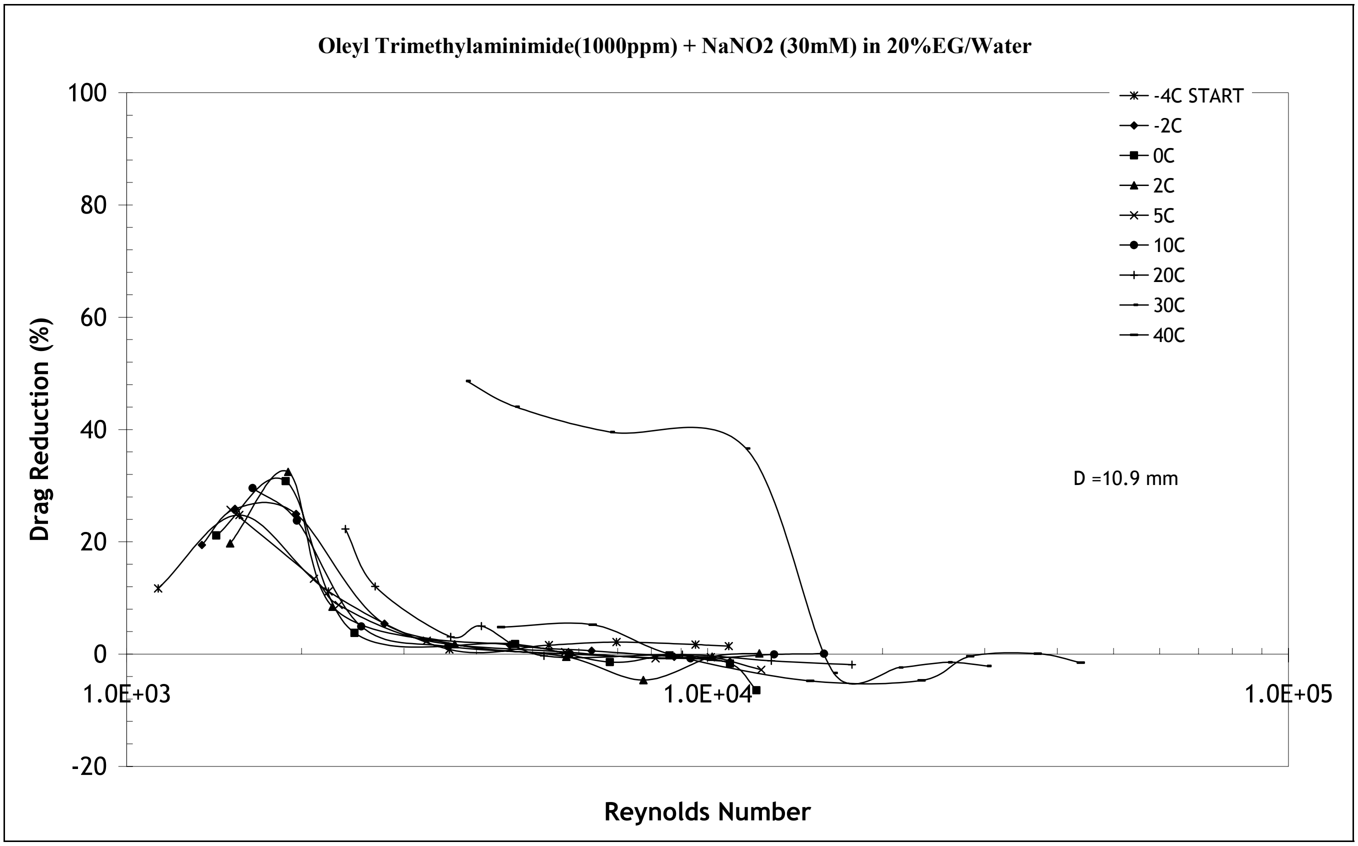


Figure 14: Oleyl Trimethylaminimide (1000 ppm) + NaNO2 (30 mM) in 20% Ethylene Glycol/Water: TEST 4

ii) <u>500 ppm</u>

The next variable studied for the oleyl trimethylaminimide was the surfactant concentration in the solution to see if the surfactant would exhibit drag reduction at lower concentrations. The first test was at 500 ppm, and as can be seen in Figure 15, the drag reduction was fairly good. The temperature range for effective drag reduction was reduced to 0 – 40°C, compared to 0 – 60 °C for 1000 ppm. Peaks were also generally less broad, but maintained nearly the same height (around 70% drag reduction for 30, 40, and 50 °C, while at 50% and 61% at 0 and 10 °C, respectively). Overall, after halving the concentration, the oleyl trimethylaminimide performed surprisingly well.

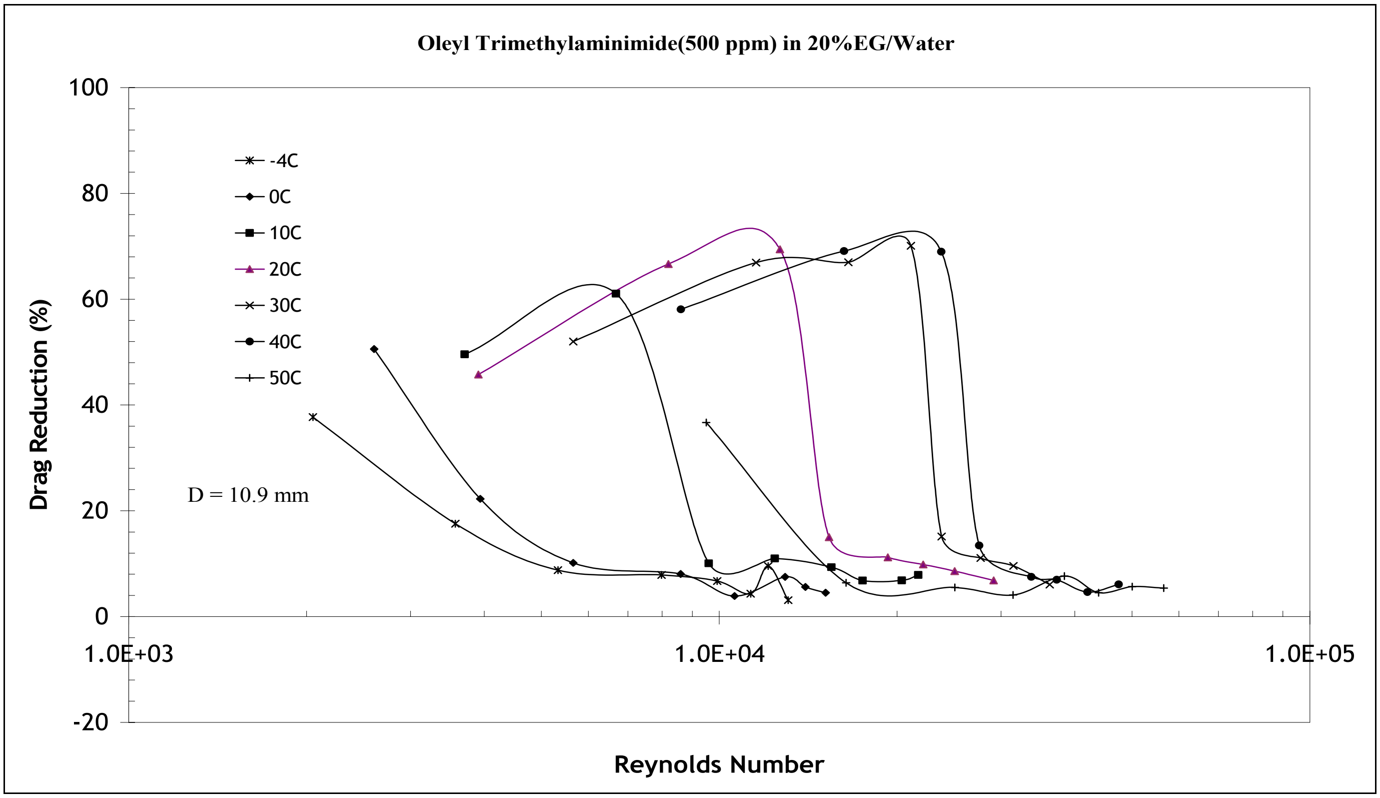


Figure 15: Oleyl Trimethylaminimide (500 ppm) in 20% Ethylene Glycol/Water

iii) <u>200 ppm</u>

The next step in the concentration study was to test oleyl trimethylaminimide at an even lower concentration (200 ppm). The results were once again surprising, as the solution continued to exhibit significant drag reduction over the temperature range of 5 – 40 °C, which can be seen in Figure 16.

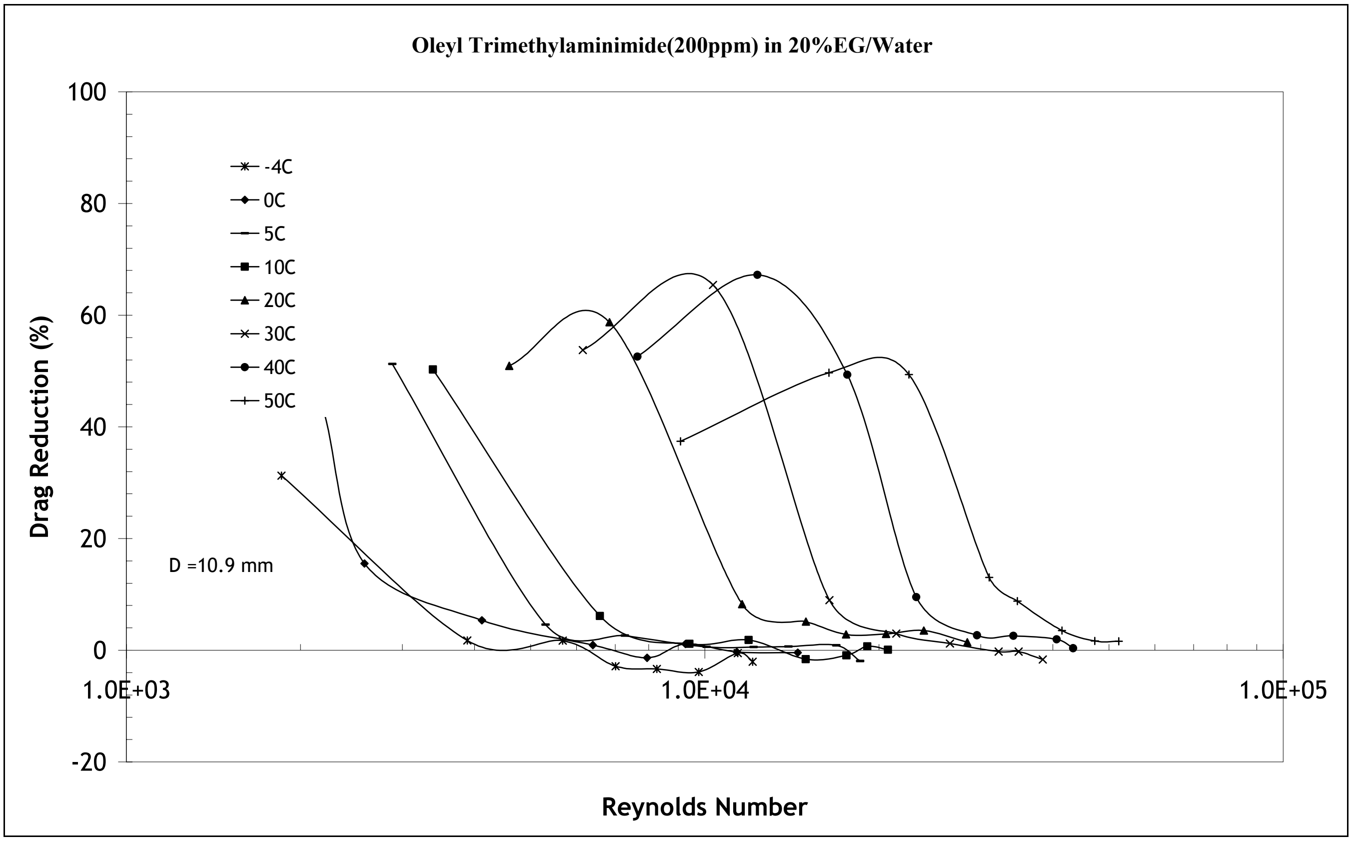


Figure 16: Oleyl Trimethylaminimide (200 ppm) in 20% Ethylene Glycol/Water

Additions of sodium nitrite were tried again with 3, 6, and 30 mM. The plots for these solutions can be seen in Figures 17, 18, and 19, respectively. The best sodium nitrite concentration was 3 mM. At this concentration lower temperature drag reduction was positively affected, yet the high temperature drag reduction decreased only slightly. At 6 and 30 mM sodium nitrite, the drag reducing behavior at high and low temperatures decreased. The effect of sodium nitrite at this concentration showed the same trends as at 1000 ppm. That is, no sodium nitrite present in solution gives the best drag reducing results, followed by a minimum amount of sodium nitrite (3 mM) being second best. As more sodium nitrite is added, the results worsen. Still, the surprising result of these experiments is that significant drag reduction was observed at such low oleyl trimethylaminimide concentrations.

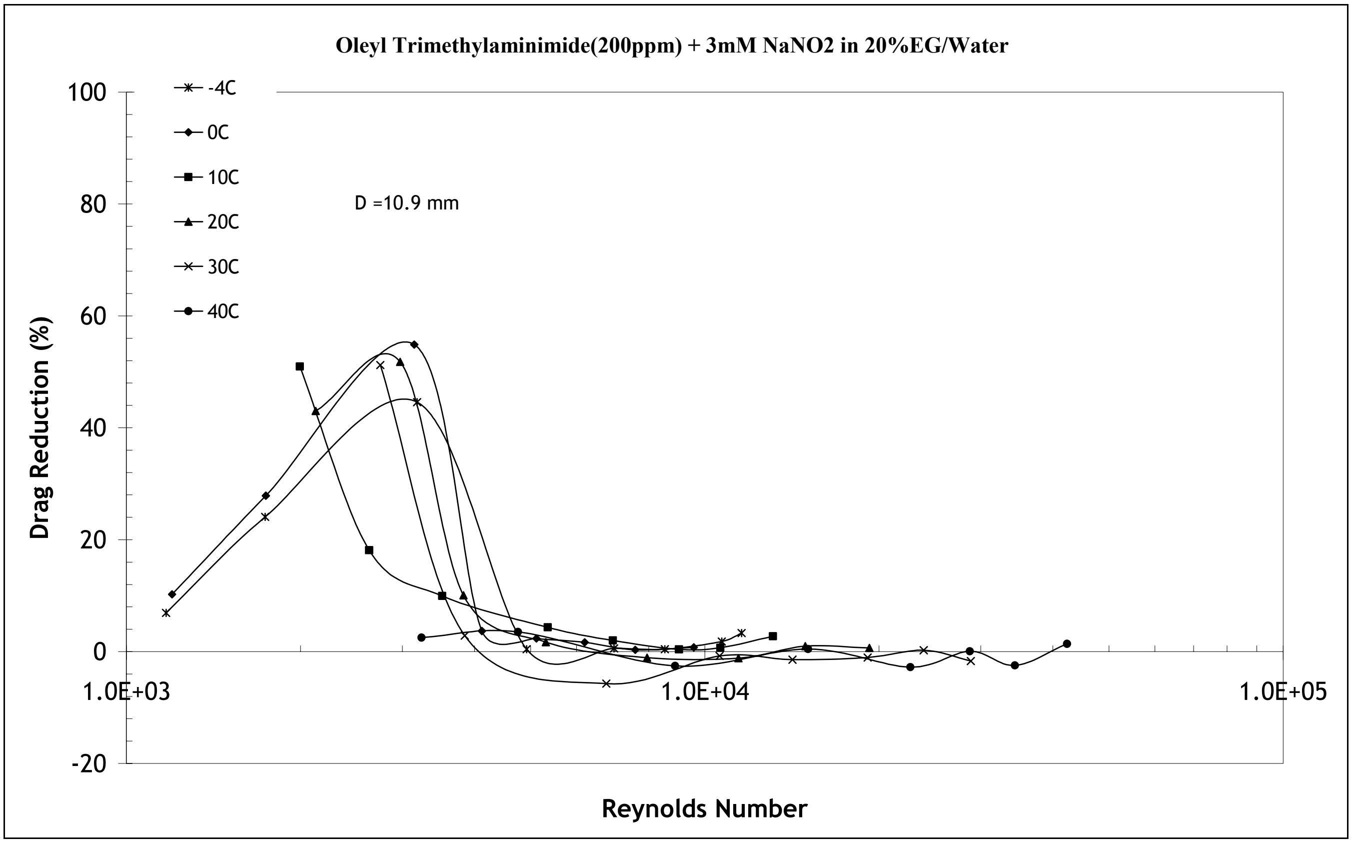


Figure 17: Oleyl Trimethylaminimide (200 ppm) + NaNO2 (3 mM) in 20% Ethylene Glycol/Water

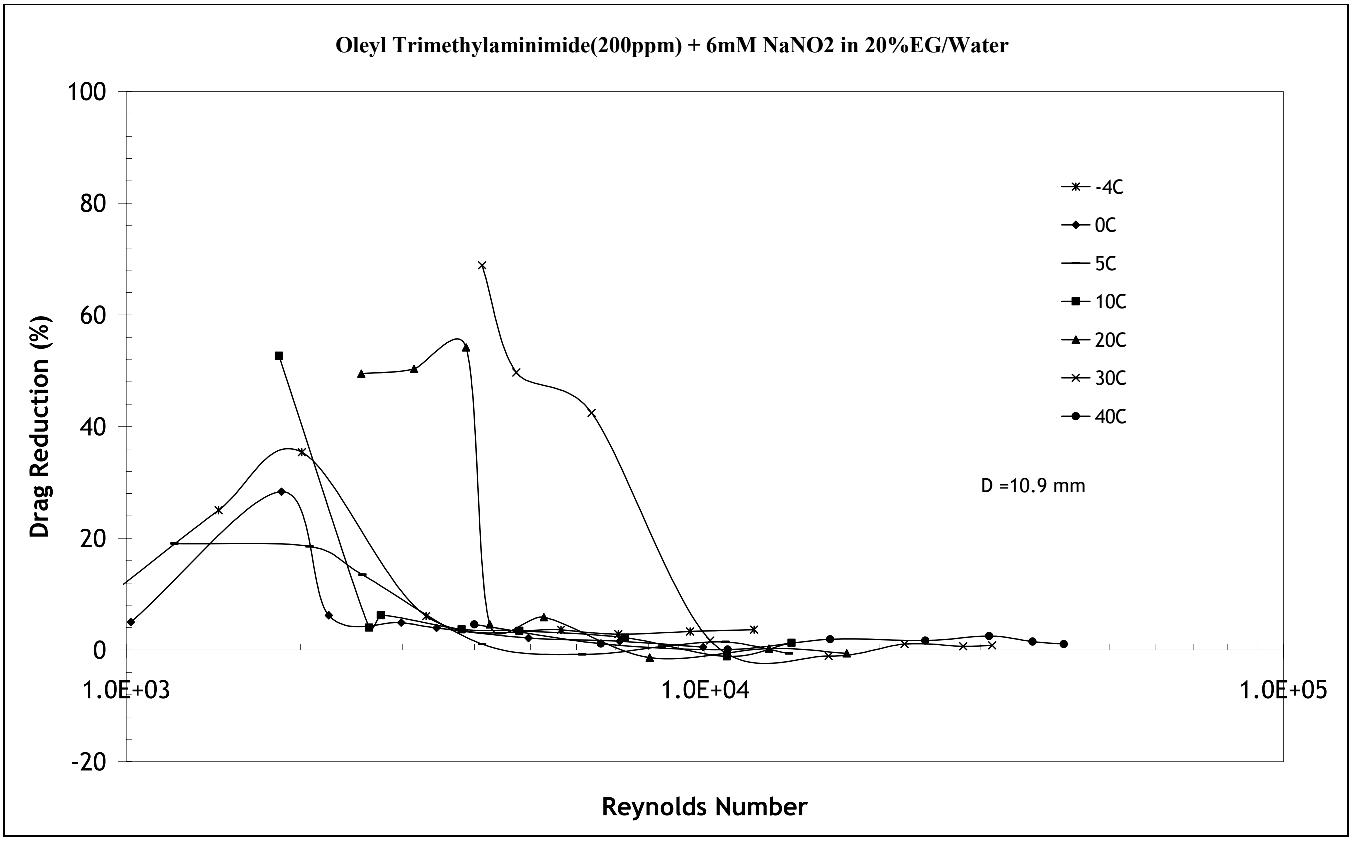


Figure 18: Oleyl Trimethylaminimide (200 ppm) + NaNO2 (6 mM) in 20% Ethylene Glycol/Water

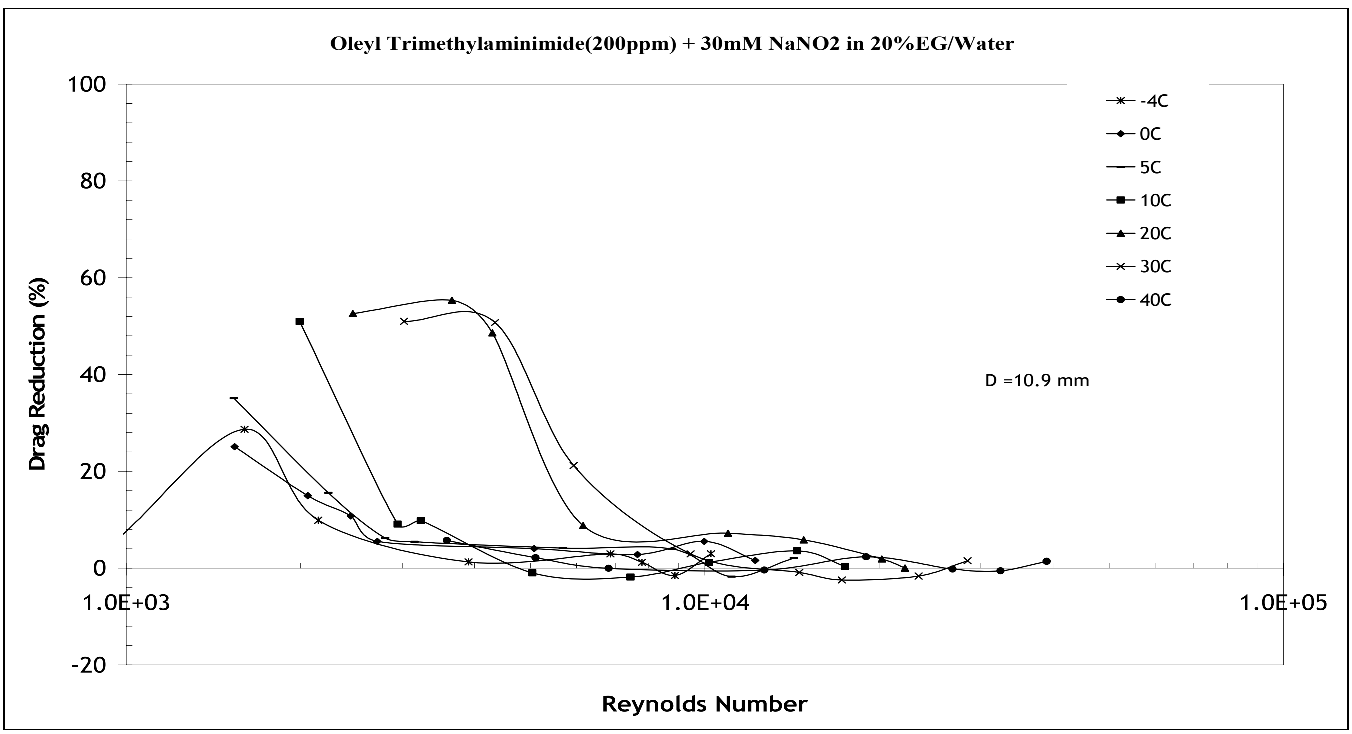


Figure 19: Oleyl Trimethylaminimide (200 ppm) + NaNO2 (30 mM) in 20% Ethylene Glycol/Water

iv) <u>50 ppm</u>

The next logical step was to try an even lower oleyl trimethylaminimide concentration. As can be seen in Figure 20, the drag reduction results were much worse than at all previous concentrations. The only significant drag reduction was observed at 40 °C. Further testing should be done to determine what the concentration limit of significant drag reduction is for oleyl trimethylaminimide.

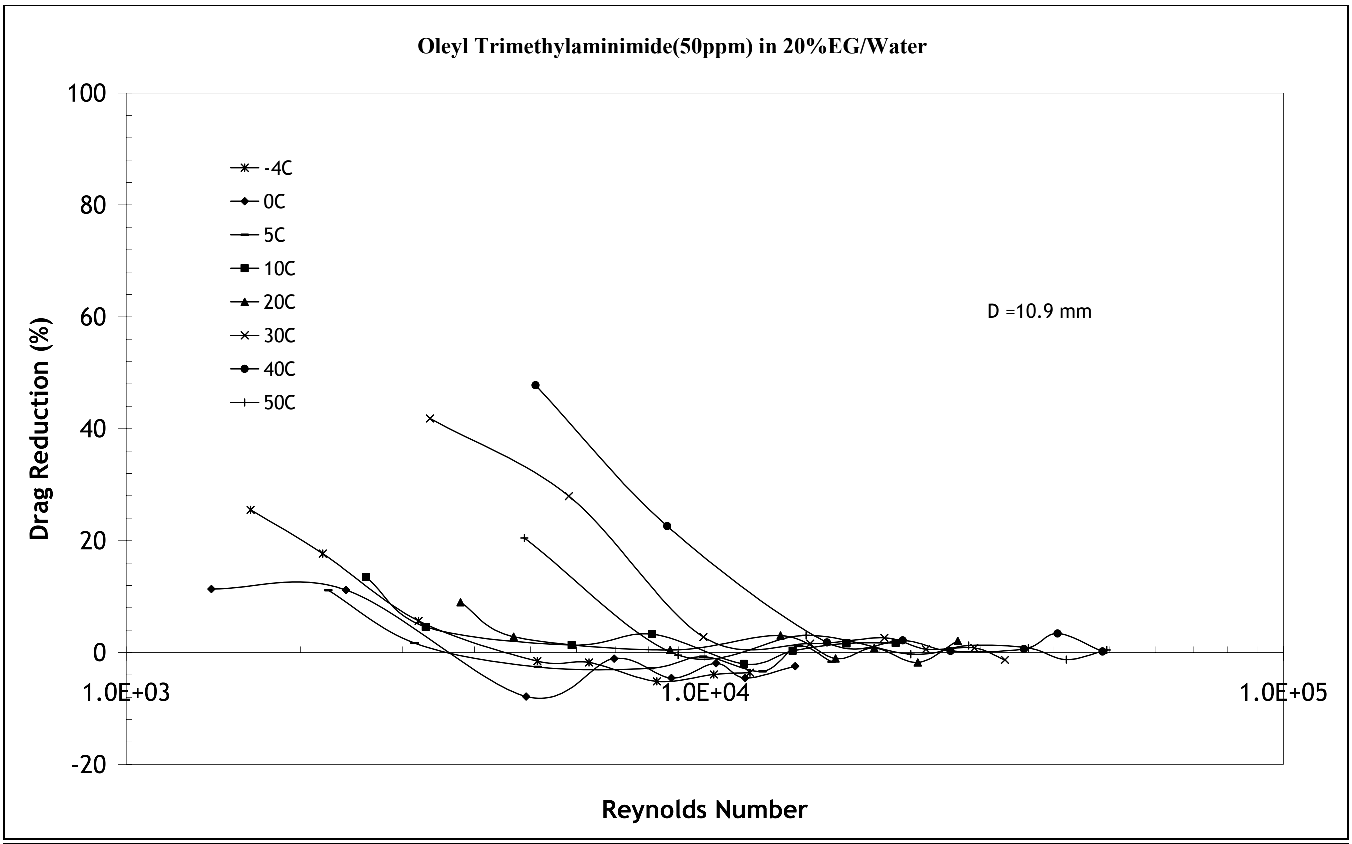


Figure 20: Oleyl Trimethylaminimide (50 ppm) in 20% Ethylene Glycol/Water

3) Oleyl Trimethylaminimide Drag Reduction Summary

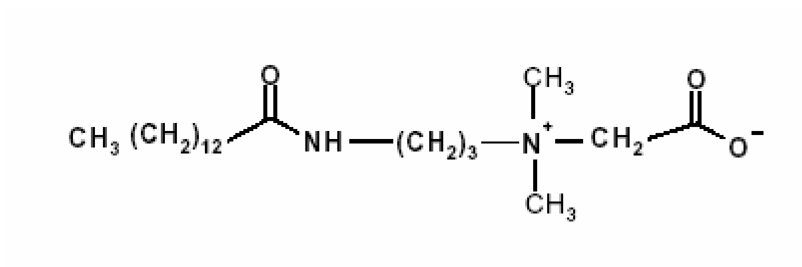
A summary of the oleyl trimethylaminimide results can be seen below in Table 3, with the significant drag reduction temperature range listed. Also, the maximum drag reduction peaks are specified at 20 °C and at low temperatures.

Table 3: Summary of Oleyl Trimethylaminimide Results

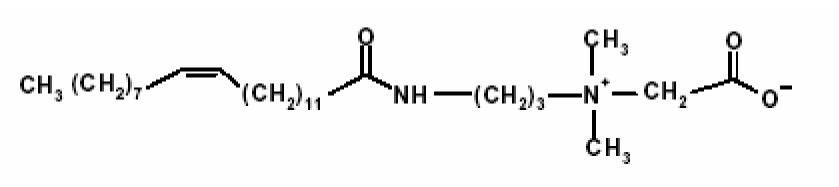
Surfactant	Surfactant Concentration (ppm)	$NaNO_2$ (mM)	Solvent	Significant DR (>50%) Temperature Range (°C)	Maximum %DR (20 °C)	Maximum %DR (Low Temperature)
Oleyl Trimethylaminimide	1000	0	Water	5 - 30	70%	59% (5°C)
Oleyl Trimethylaminimide	1000	0	20% EG/Water	0 - 60	72%	14% (-4°C); 53% (0°C)
Oleyl Trimethylaminimide	1000	3	20% EG/Water	0 - 40	71%	23% (-4°C); 51% (0°C)
Oleyl Trimethylaminimide	1000	6	20% EG/Water	0 - 40	54%	37% (-4°C); 50% (0°C)
Oleyl Trimethylaminimide (same solution as lower NaNO2 concentrations)	1000	30	20% EG/Water	-4 - 30	54%	68% (-4°C); 50% (0°C)
Oleyl Trimethylaminimide (retest of this solution with emphasis around 0°C)	1000	30	20% EG/Water	-4, 10 - 20	56%	50% (-4°C); 40% (-2°C); 47% (0°C)
Oleyl Trimethylaminimide (fresh solution prepared)	1000	30	20% EG/Water	-4	15%	61% (-4°C START); 27% (-4°C END); 26% (-2°C); 24% (0°C)
Oleyl Trimethylaminimide (retesting of fresh solution)	1000	30	20% EG/Water	-	22%	25% (-4°C); 26% (-2°C); 31% (0°C)
Oleyl Trimethylaminimide	500	0	20% EG/Water	0 - 40	69%	38% (-4°C); 51% (0°C)
Oleyl Trimethylaminimide	200	0	20% EG/Water	5 - 40	59%	31% (-4°C); 43% (0°C)
Oleyl Trimethylaminimide	200	3	20% EG/Water	0 - 30	52%	45% (-4°C); 55% (0°C)
Oleyl Trimethylaminimide	200	6	20% EG/Water	10 - 30	54%	35% (-4°C); 28% (0°C)
Oleyl Trimethylaminimide	200	30	20% EG/Water	10 - 30	55%	29% (-4°C); 25% (0°C)
Oleyl Trimethylaminimide	50	0	20% EG/Water	-	9%	26% (-4°C)

B) DR0206

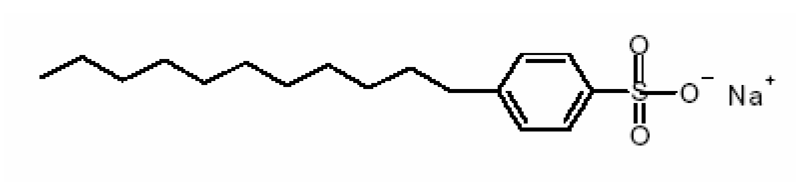
DR0206 is a commercial surfactant, manufactured by Akzo Nobel, consisting of a mix of zwitterionic and anionic surfactants. The components are shown in Figure 21 with their respective structures, classifications, and molar composition percentages.



Myristylamidopropylbetaine (20%, Zwitterionic)



Rapeseedamidopropylbetaine (10%, Zwitterionic)



Alkyl Benzene Sulphonic Acid, Sodium Salt (5 %, Anionic)

Figure 21: Composition and Structure of DR0206

1) Water

DR0206 was first tested at a concentration of 4 g/L in water. It exhibited significant drag reduction in the temperature range of 20 – 50 °C. The peaks became broader and higher (around 70%) at the higher temperatures (40 and 50 °C), while at lower temperatures they dropped off more quickly and had lower peaks (around 50 to 60%). The trends can be seen in Figure 22.

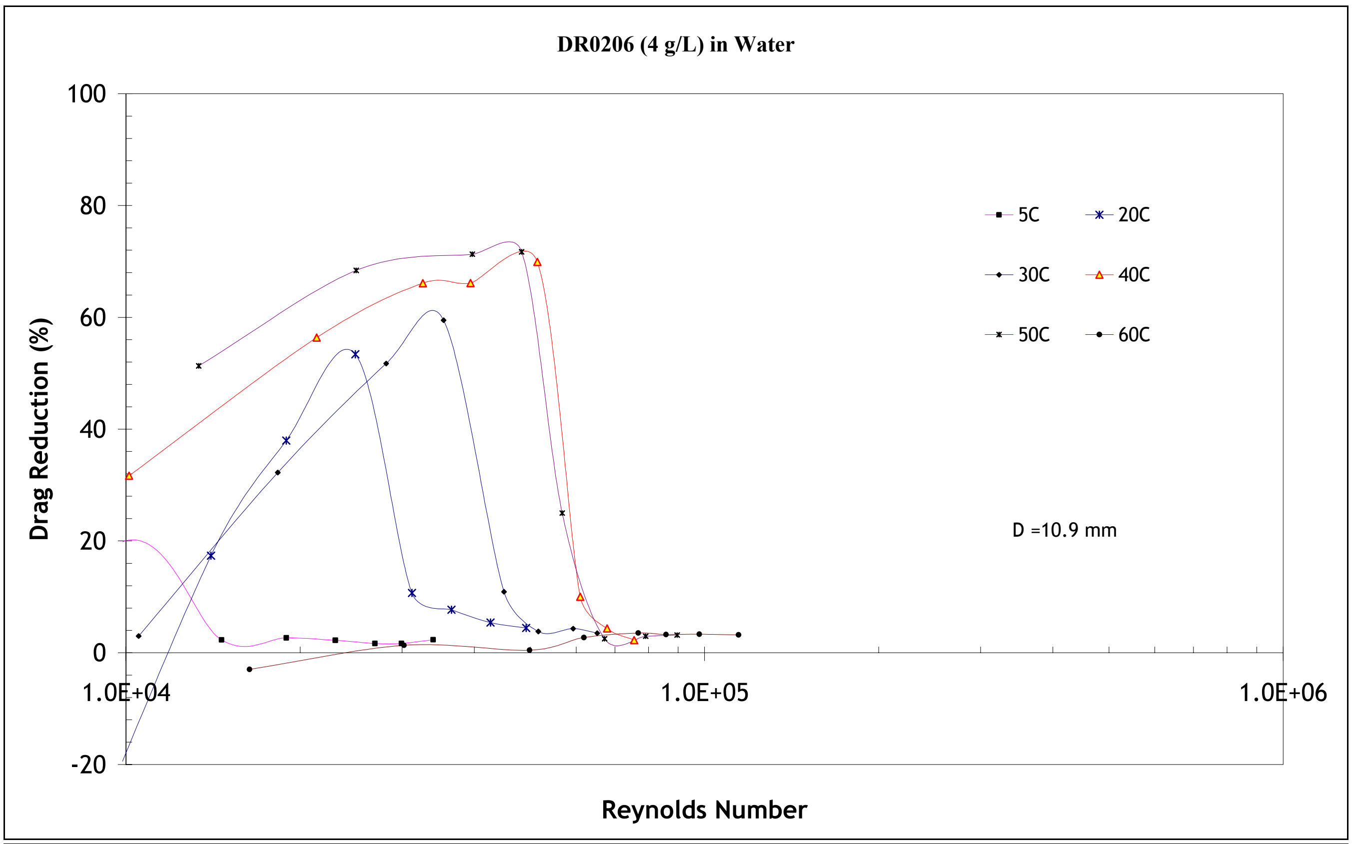


Figure 22: DR0206 (4 g/L) in Water

The addition of 30 mM of sodium nitrite caused a change in the drag reducing behavior at higher temperatures. The significant drag reduction temperature range was extended from 20 – 50 °C to 20 – 60 °C. Other than this, the broadness and height of the peaks all remained the same, which can be seen in Figure 23.

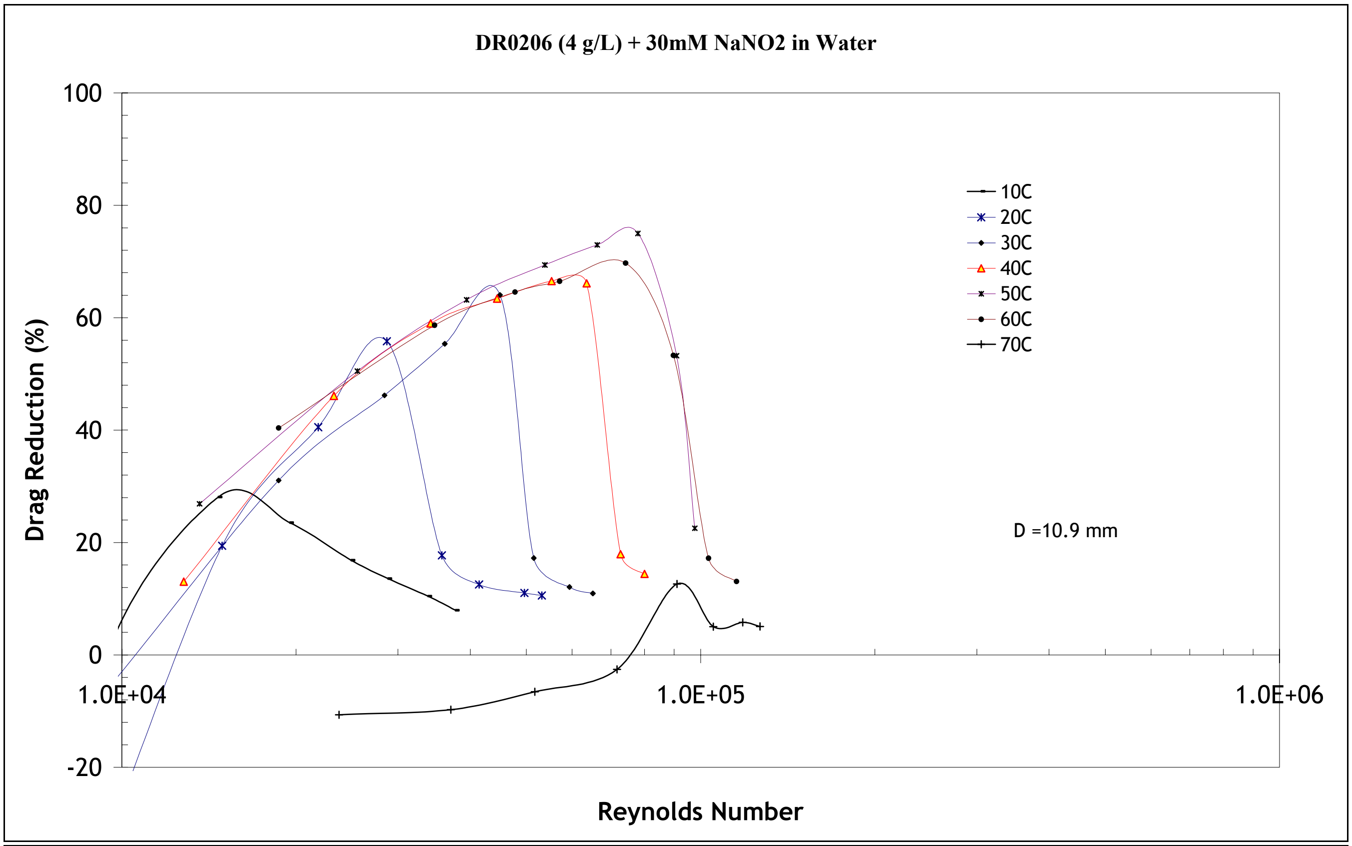


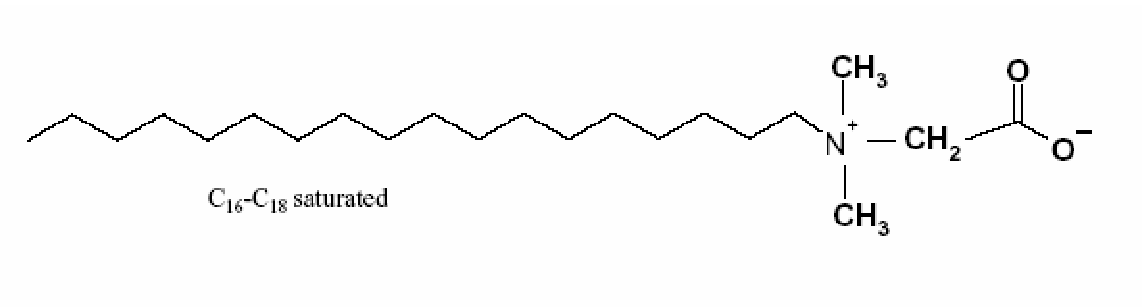
Figure 23: DR0206 (4 g/L) + NaNO2 (30 mM) in Water

2) 20% Ethylene Glycol/Water

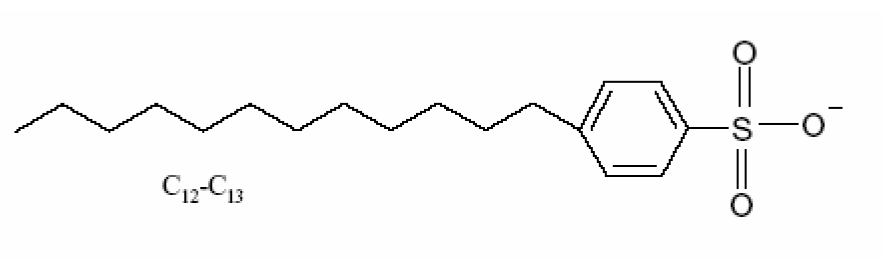
DR0206 was also tested in 20% ethylene glycol/water at 4 g/L. Unfortunately, no significant drag reduction was observed, and nearly all points were along the 0% drag reduction line. This was consistent for all temperatures tested (-4 to 50 °C). The plots of these solutions can be found in Appendix A

C) SPE98300

Like DR0206, SPE98300 is a commercial surfactant manufactured by Akzo Nobel that consists of zwitterionic and anionic surfactants. The components are shown in Figure 24 with their respective structures, classifications, and molar compositions. In addition to these active components, the solution also contains 33% water and 30% isopropanol (by weight).



Alkylbetaine (27%, Zwitterionic)



Alkylbenzene Sulphonate (6.7 %, Anionic)

Figure 24: Components and Structure of SPE98300

The SPE98300 was used at a concentration of 1500 ppm of the active ingredients, which are the zwitterionic and anionic surfactants mentioned above. Two other additives were combined with this surfactant, Trilon A at a concentration of 500 ppm and formaldehyde at a concentration of 130 ppm. Their structures are in Figures 25 and 26. Trilon A is a sequestering agent that combines with metal ions and formaldehyde is a biocide.

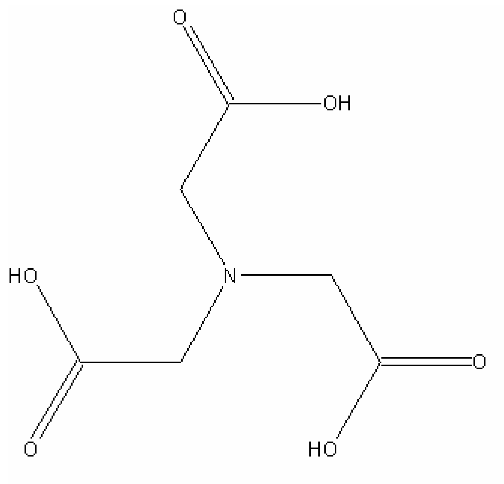


Figure 25: Structure of Trilon A

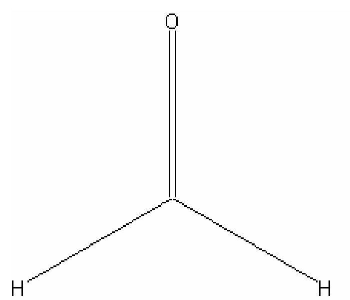


Figure 26: Structure of Formaldehyde

The surfactant and additive combination was tested in three different solvents (water, 20% ethylene glycol/water, and 30% glycerol/water) and with and without the addition of sodium nitrite.

1) Water

The combination of SPE98300 (1500 ppm – active), Trilon A (500 ppm), and formaldehyde (130 ppm) was first tested in water. As can be seen in Figure 27, the solution exhibited significant drag reducing behavior in the temperature range of 30 to 60 °C. The peaks in this range started at 53% at 30 °C, went up to 65% at 40°C, and up to

75% and 77% at 50 and 60 °C, respectively. At lower temperatures, the peak at 5 °C was around 25% while the peak at 20 °C was around 44%. The peaks dropped off quickly at low temperatures and broadened somewhat at higher temperatures.

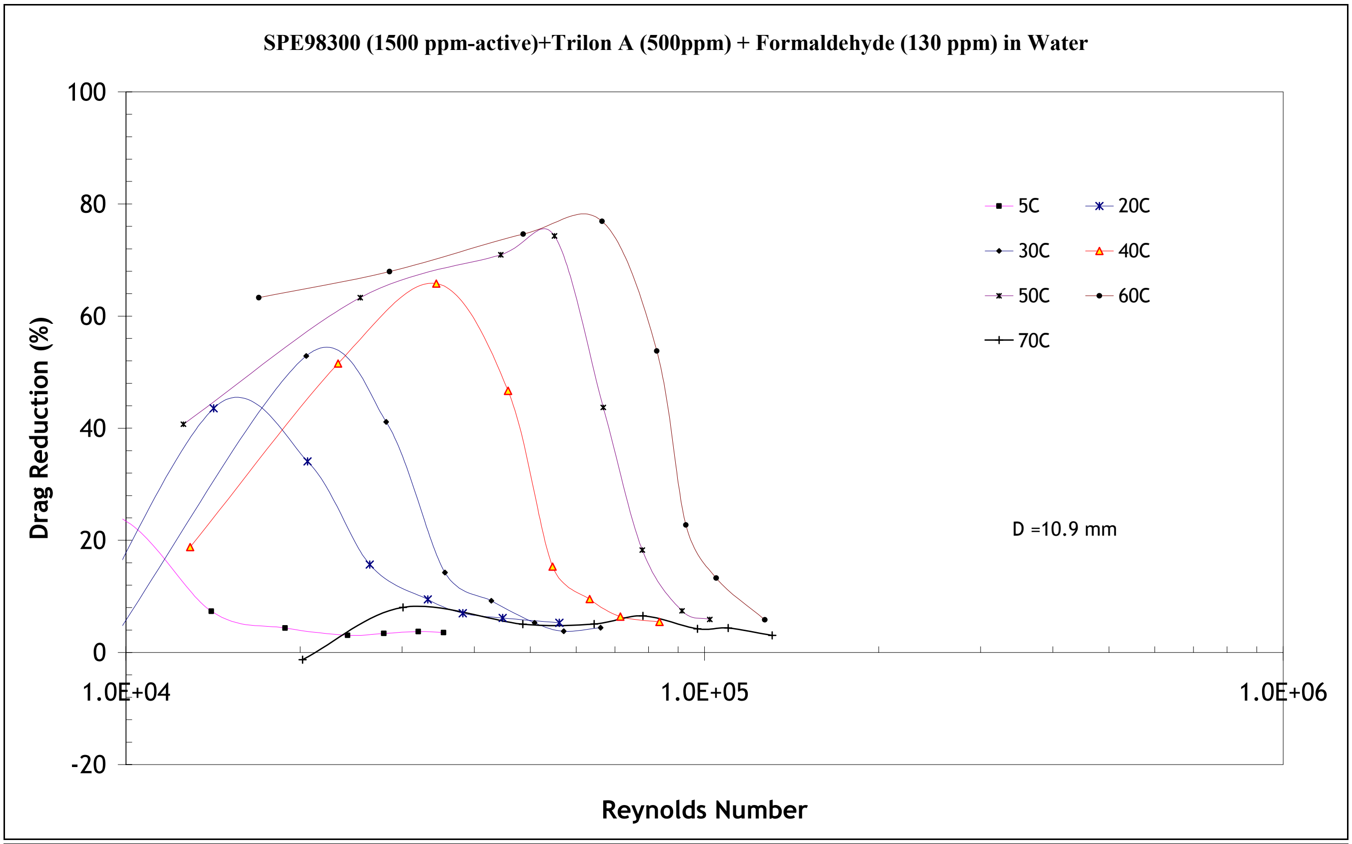


Figure 27: SPE98300 (1500 ppm - active) + Trilon A (500 ppm) + Formaldehyde (130 ppm) in Water

Addition of 30 mM sodium nitrite caused the temperature range of significant drag reduction to extend to lower temperatures (20 °C) and high temperatures (70 °C). All of the peaks increased slightly in height, while the quick drop offs remained. At 60 °C the peak reached 78%. Overall, the addition of sodium nitrite to this solution benefited its drag reducing behavior. The trends can be seen in Figure 28.

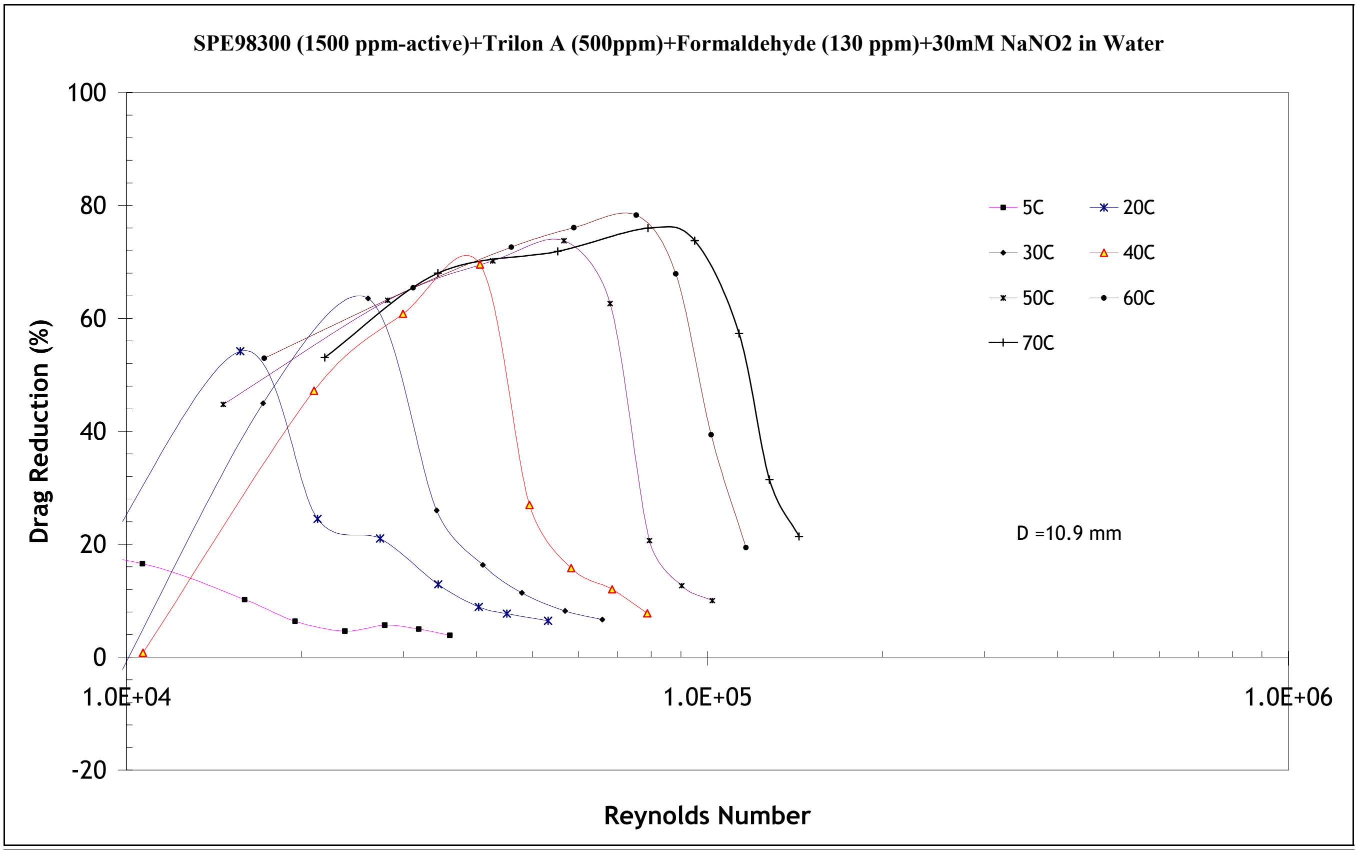


Figure 28: SPE98300 (1500 ppm - active) + Trilon A (500 ppm) + Formaldehyde (130 ppm) + NaNO2 (30 mM) in Water

2) <u>20% Ethylene Glycol/Water</u>

The next solvent that this surfactant system was tested in was 20% ethylene glycol and water. The drag reduction results of this solution were much worse than those in water. Significant drag reduction was not reached in this solution, although a peak at 20 °C came close with 42% drag reduction. The trends can be seen in Figure 29.

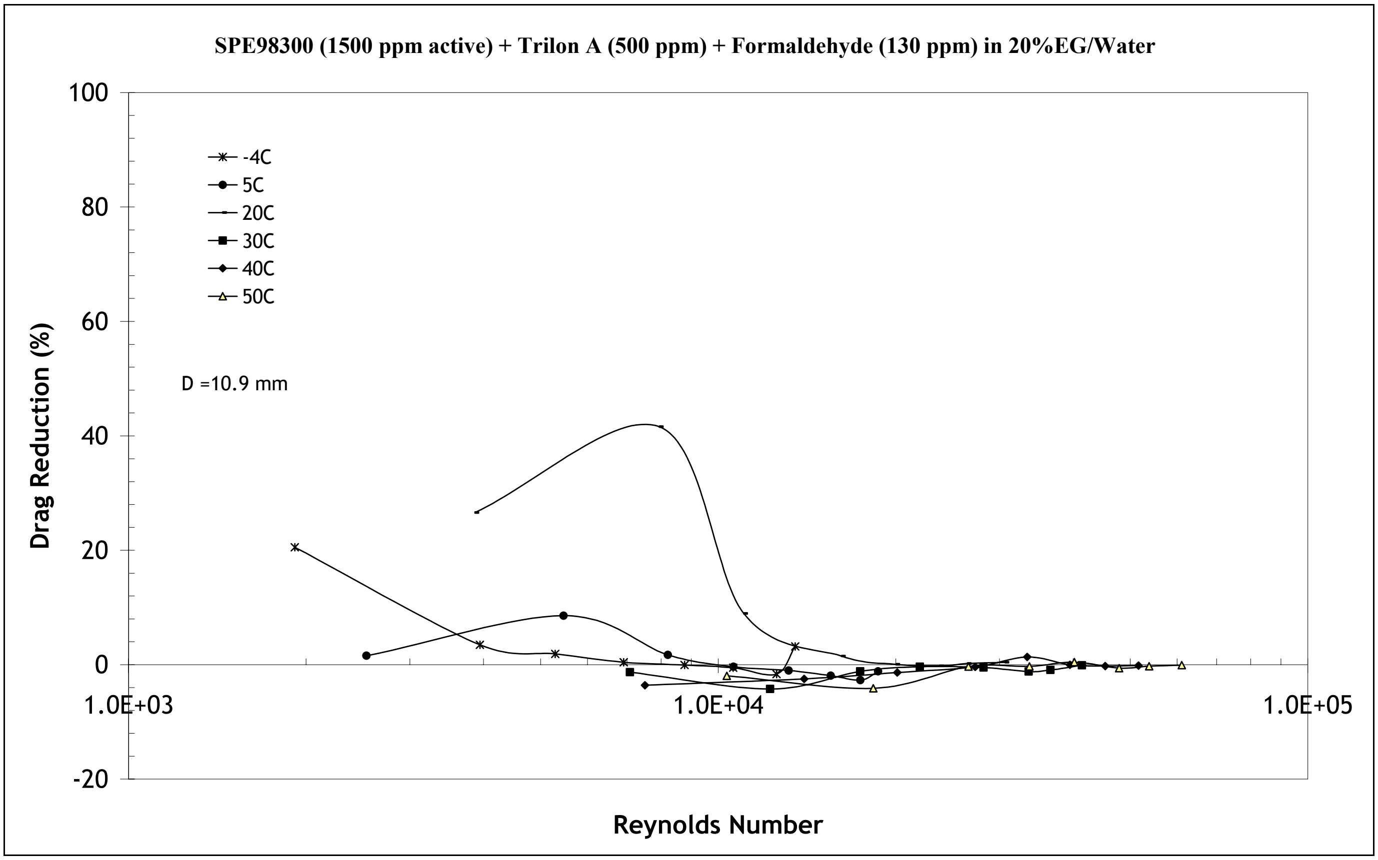


Figure 29: SPE98300 (1500 ppm - active) + Trilon A (500 ppm) + Formaldehyde (130 ppm) in 20% Ethylene Glycol/Water

The addition of 30 mM sodium nitrite improved the results slightly, but not enough to consider this surfactant in 20% ethylene/glycol a promising solution. Significant drag reduction was reached at 30 °C, with a peak of 57%. A peak at 20 °C reached 36%, while a peak at 5 °C reached 29%. These trends can be seen in Figure 30.

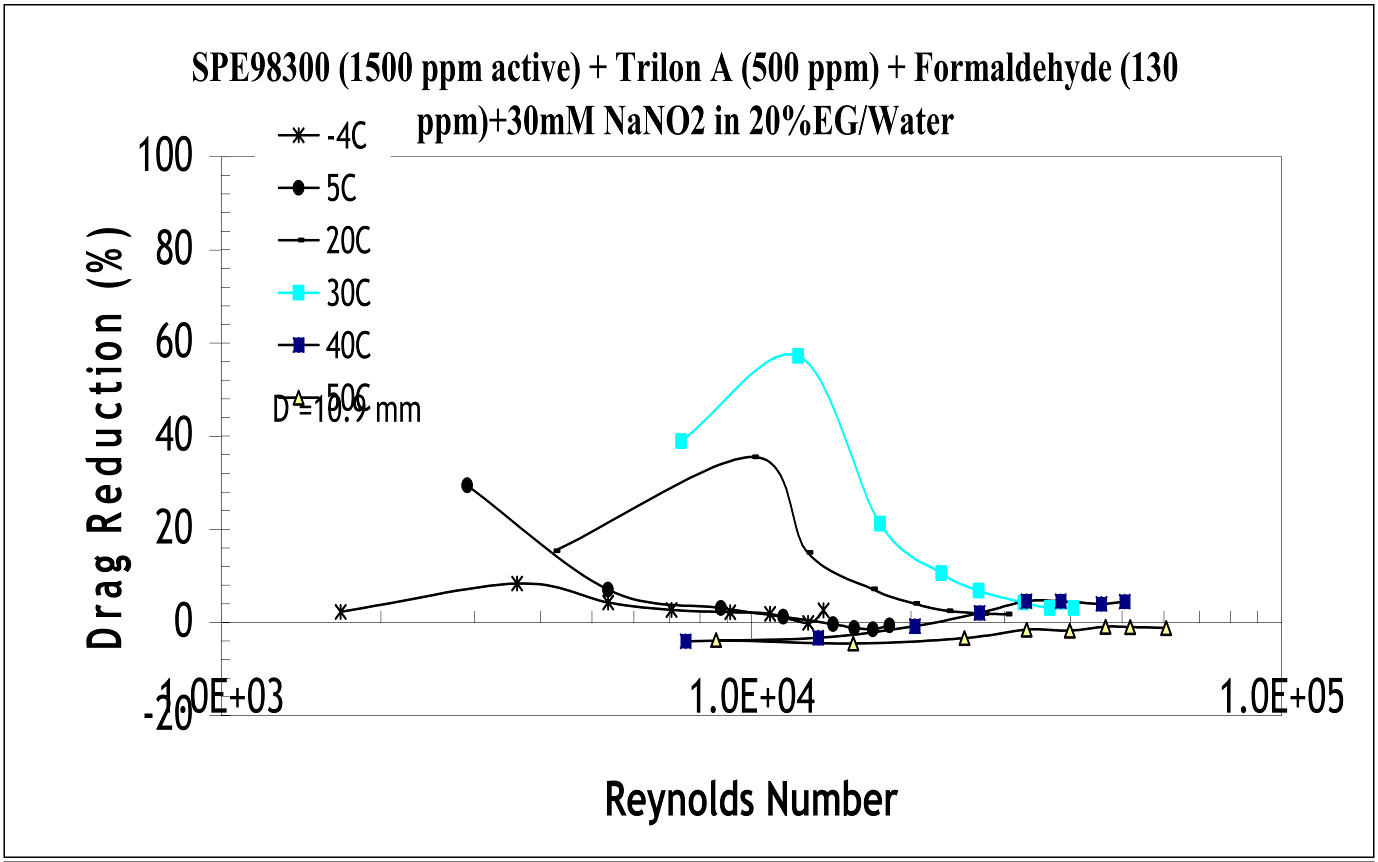


Figure 30: SPE98300 (1500 ppm - active) + Trilon A (500 ppm) + Formaldehyde (130 ppm) + 30 mM NaNO2 in 20% Ethylene Glycol/Water

3) <u>30% Glycerol/Water</u>

The final solvent the components were tested in was 30% glycerol and water. Significant drag reduction was reached at 30 and 40 °C with peaks at 62% and 52%, respectively. At 20 °C a peak of 36% was reached. These peaks were relatively narrow, and for the most part, this solution had poor drag reducing behavior. Figure 31 is the plot for this solution.

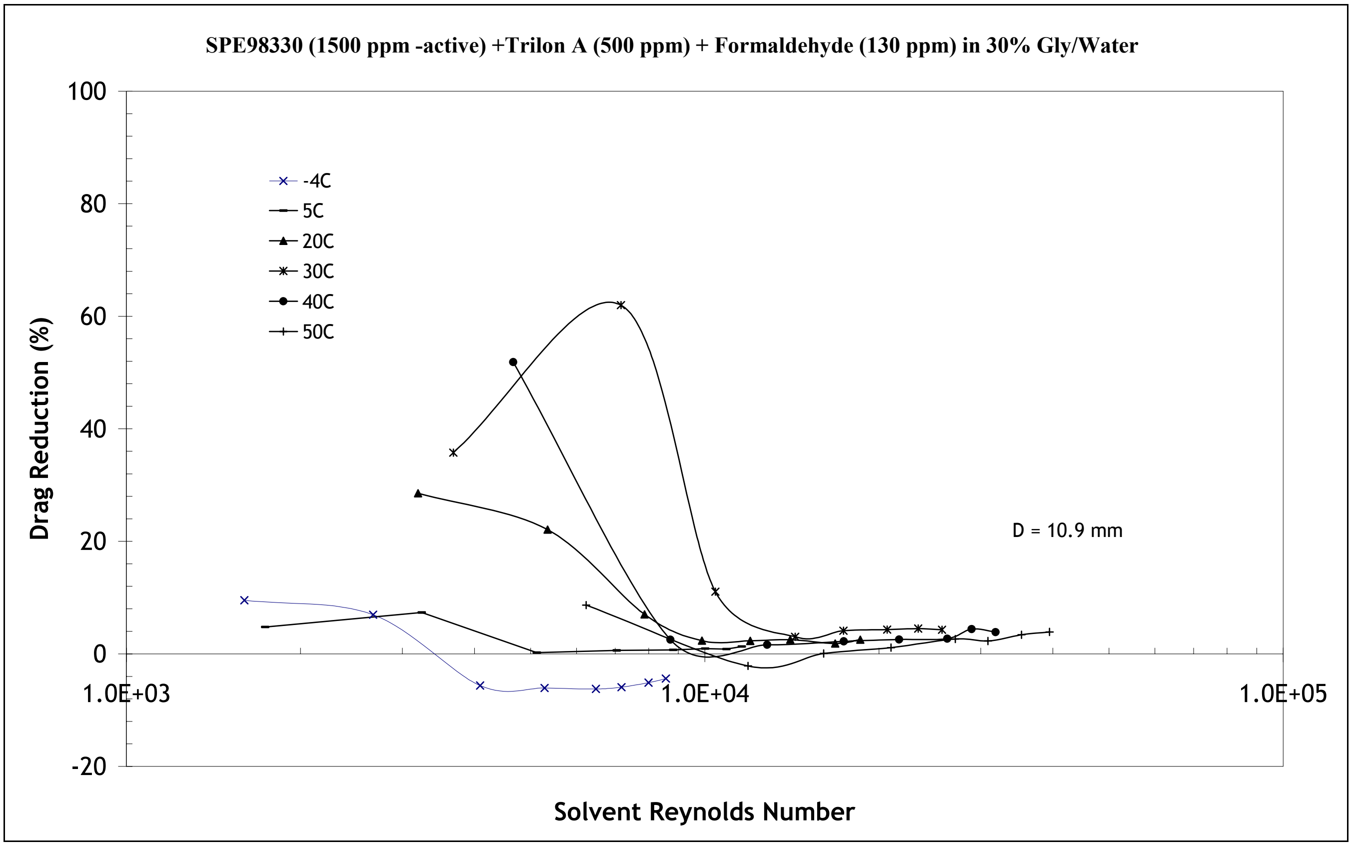


Figure 31: SPE98300 (1500 ppm - active) + Trilon A (500 ppm) + Formaldehyde (130 ppm) in 30% Glycerol/Water

The addition of 30 mM sodium nitrite to this solution in 30% glycerol/water was then tested. The drag reducing behavior observed was surprisingly improved, with the significant drag reduction temperature range of 20 to 50 °C. Peaks were more established in this plot, and at 5 °C a peak of 47% was reached. Figure 32 shows the trends for this solution.

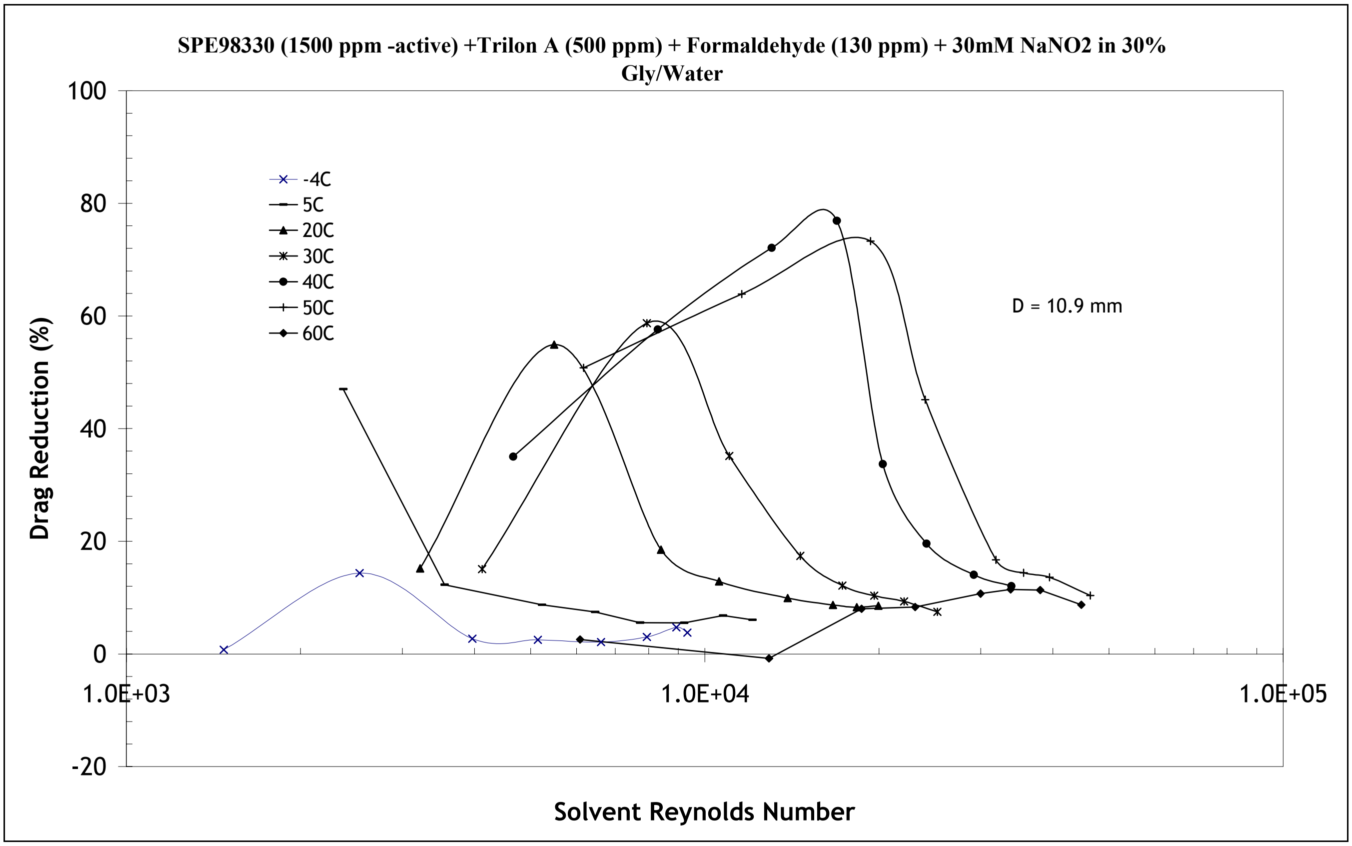


Figure 32: SPE98300 (1500 ppm - active) + Trilon A (500 ppm) + Formaldehyde (130 ppm) + NaNO2 (30 mM) in 30% Glycerol/Water

4) <u>SPE98300 Summary</u>

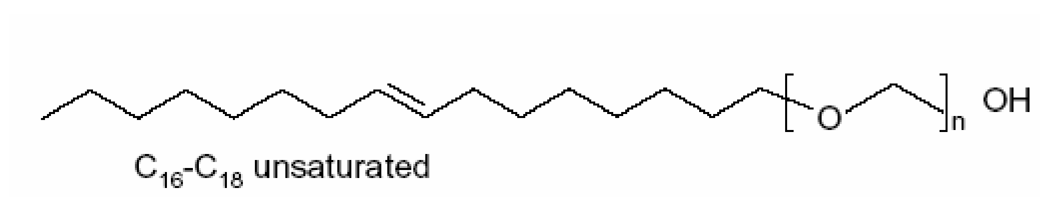
A summary of the SPE98300 results can be seen in Table 4, with the significant drag reduction temperature ranges listed. Also, the maximum drag reduction peaks are specified at 20 °C and at low temperatures. Overall, the addition of sodium nitrite (30 mM) to all solutions (three solvents) gave significantly better drag reducing behavior.

Table 4: Summary of SPE98300 Drag Reduction Results

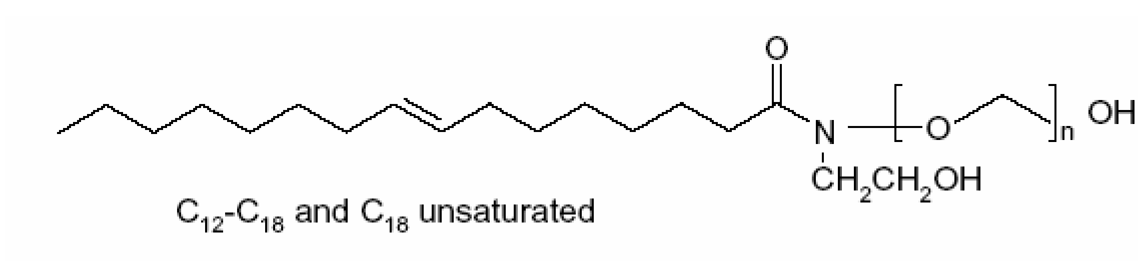
Surfactant	Surfactant Concentration (ppm)	$NaNO_2$ (mM)	Solvent	Significant DR (>50%) Temperature Range (°C)	Maximum %DR (20 °C)	Maximum %DR (Low Temperature)
SPE98300/ Trilon A /Formaldehyde	1500 (active) / 300 / 130	0	Water	30 - 60	44%	25% (5°C)
SPE98300/ Trilon A /Formaldehyde	1500 (active) / 300 / 130	30	Water	20 - 70	54%	21% (5°C)
SPE98300/ Trilon A /Formaldehyde	1500 (active) / 300 / 130	0	20% EG/Water	-	42%	21% (-4°C); 9% (5°C)
SPE98300/ Trilon A /Formaldehyde	1500 (active) / 300 / 130	30	20% EG/Water	30	36%	8% (-4°C); 29% (5°C)
SPE98300/ Trilon A /Formaldehyde	1500 (active) / 300 / 130	0	30% Gly/Water	30 - 40	29%	10% (-4°C); 7% (5°C)
SPE98300/ Trilon A /Formaldehyde	1500 (active) / 300 / 130	30	30% Gly/Water	20 - 50	55%	14% (-4°C); 47% (5°C)

D) Beraid DR DC 620

Beraid DR DC 620, a commercial non-ionic surfactant manufactured by Akzo Nobel, is actually a combination of two non-ionic surfactants. The components are shown in Figure 33 with their respective structures and molar compositions.



Alcohol Ethoxylate (50%)



Alkyl Monoethanolamide Ethoxylate (50%)

Figure 33: Structure of Beraid DR DC 620

The solvents studied with this surfactant were water, 20% ethylene glycol/water, 30% glycerol/water, and 25% propylene glycol/water. The effect of sodium nitrite (30 mM) additions was also tested.

1) <u>Water</u>

The first solvent in which Beraid DR DC 620 was tested was water, with a 1.0 wt. % concentration. The results were very good, with significant drag reduction observed in the temperature range of 5 to 40 °C. At 5 °C, the peak was 58%, and there was a drop off after this peak. For temperatures of 20 °C to 50 °C, the drag reduction continued to increase as the Reynolds number/flow rate increased, and no drop off was observed in the Reynolds number range that could be achieved. The highest peaks were at 20 and 30 °C, with 71% and 66% drag reduction, respectively. These trends can be observed in Figure 34.

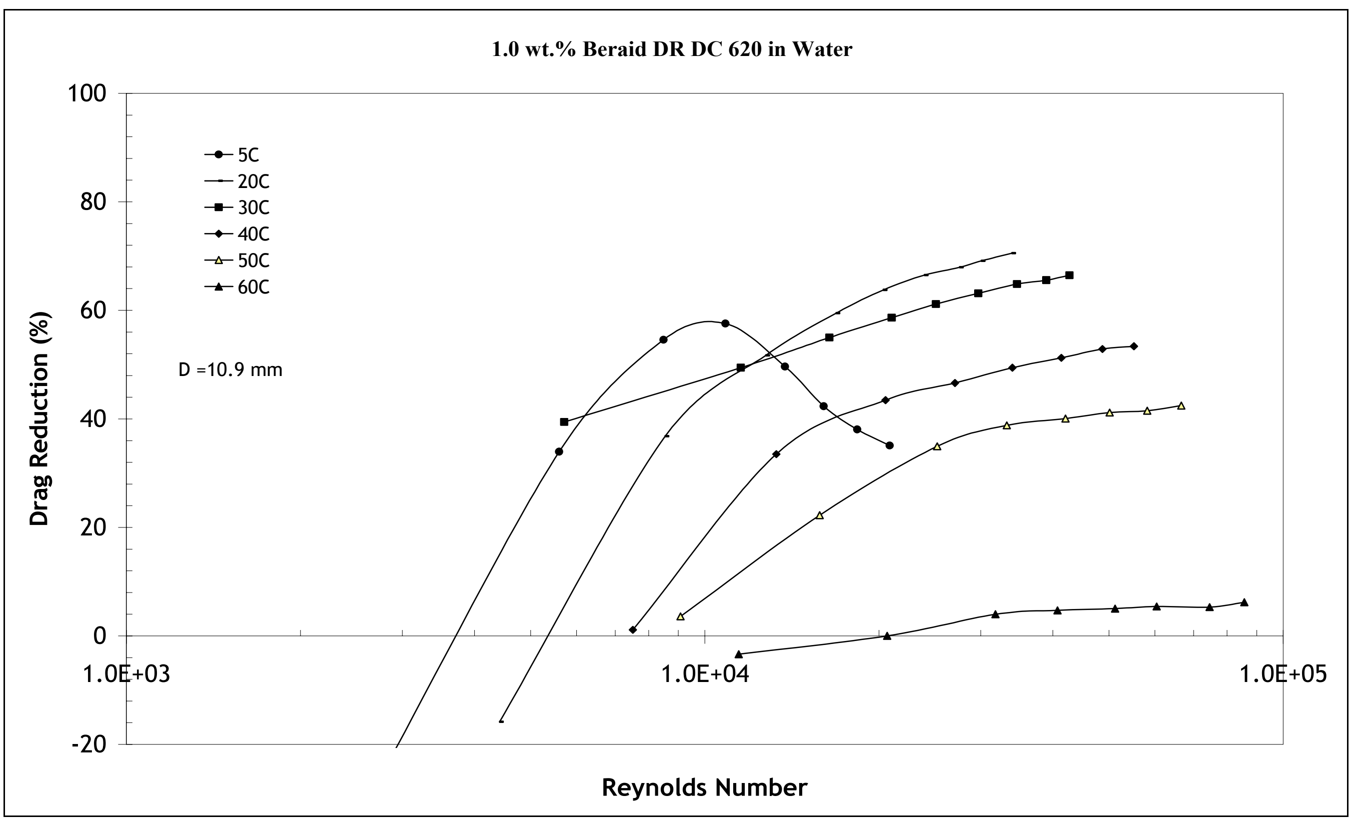


Figure 34: Beraid DR DC 620 (1.0 wt.%) in Water

An experiment was then performed with addition of 30 mM sodium nitrite to the Beraid DR DC 620 solution in water. The drag reducing behavior was nearly identical to those without sodium nitrite, with trends and peaks being similar. The significant drag reduction temperature range was therefore the same (5 – 40 °C). These similarities can be seen in Figure 35.

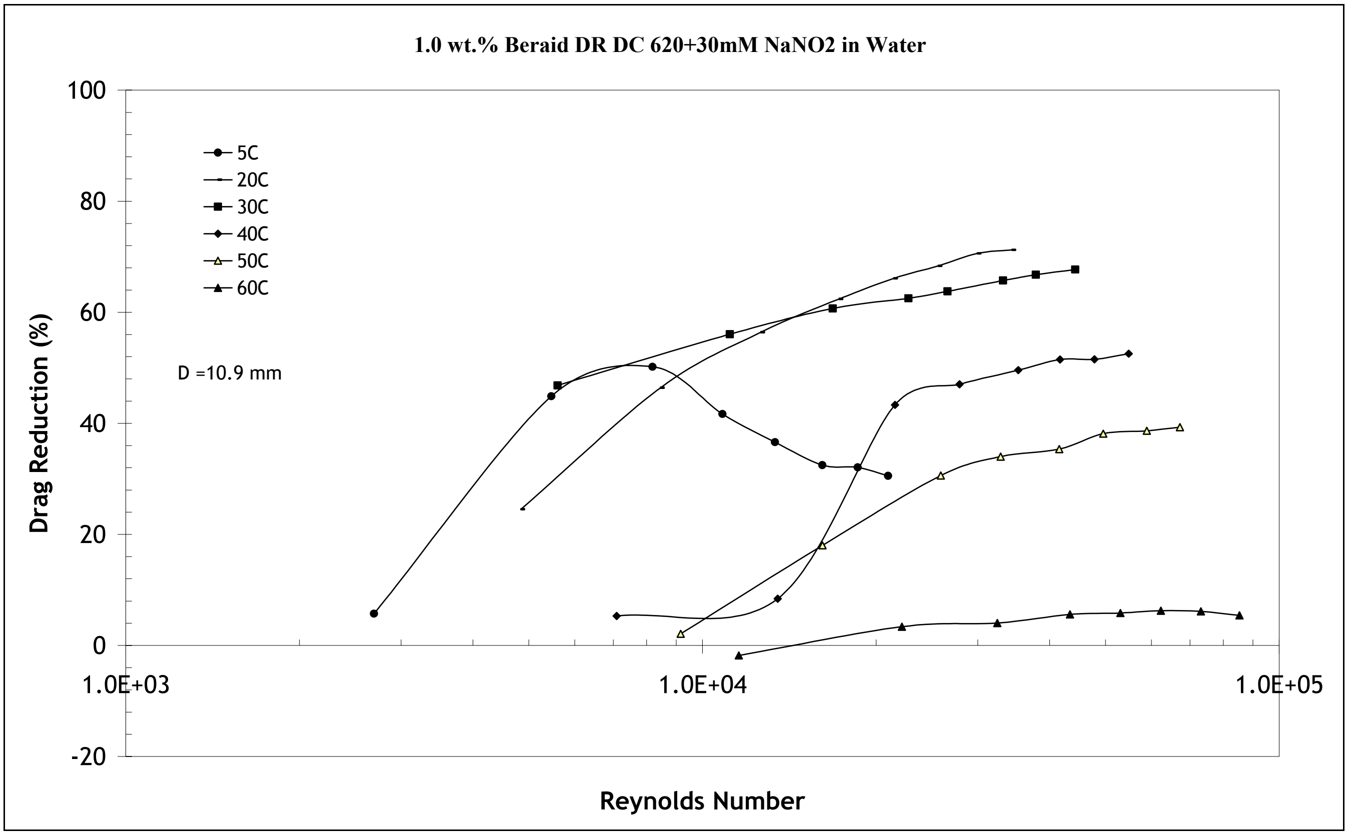


Figure 35: Beraid DR DC 620 (1.0 wt.%) +NaNO2 (30 mM) in Water

2) <u>20% Ethylene Glycol/Water</u>

The next solvent in which Beraid DR DC 620 was tested was 20% ethylene glycol/water. Significant drag reduction occurred in the temperature range of 5 to 20 °C. In this range, the peaks did not drop off. The highest peaks were at 5 and 20 °C, with maximum drag reduction of 59% and 62%, respectively. At -4 °C, the drag reduction peaked at 30% while at 30 °C it reached 46% and might exceed 50% at higher Reynolds numbers. The trends for this solution can be seen in Figure 36.

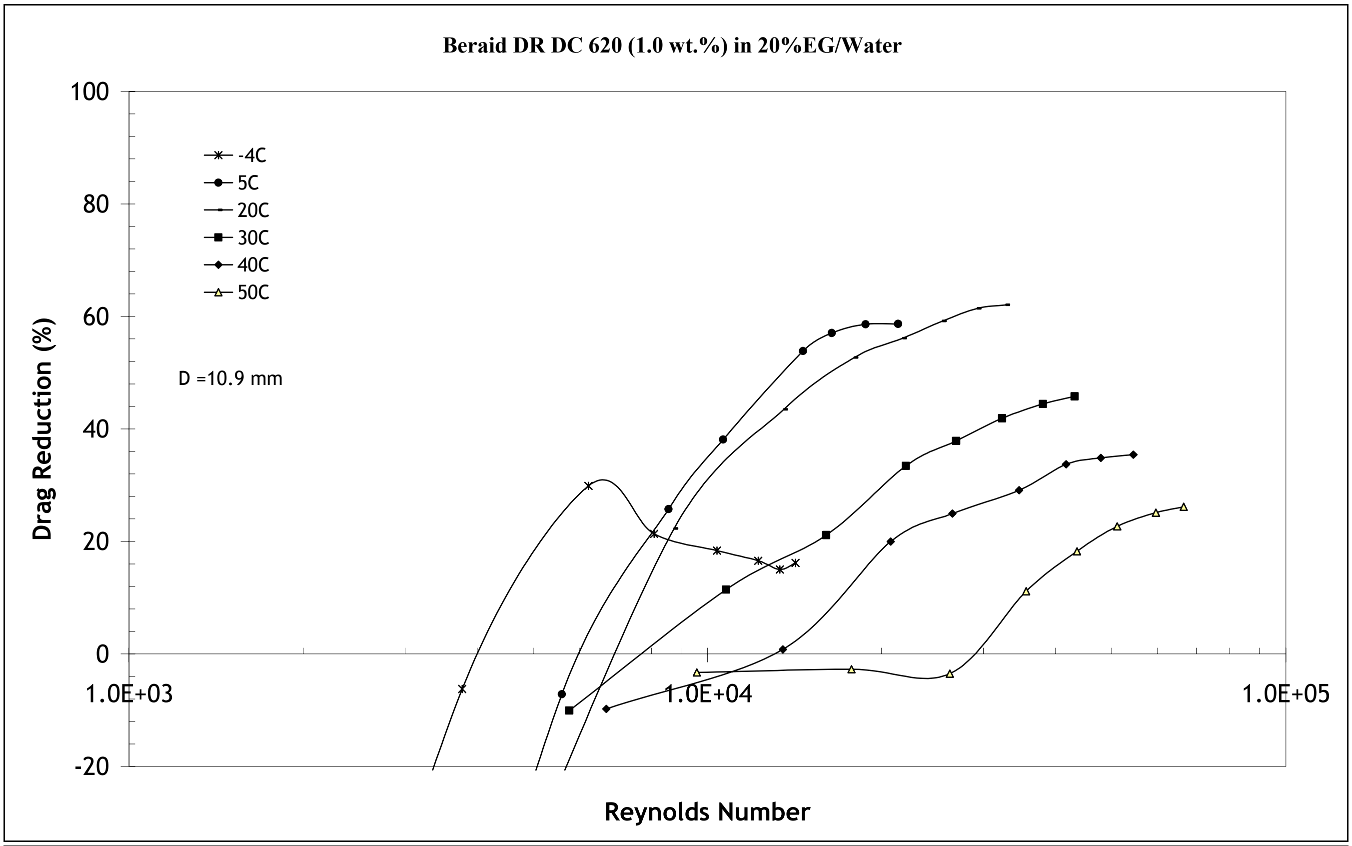


Figure 36: Beraid DR DC 620 (1.0 wt.%) in 20% Ethylene Glycol/Water

With the addition of 30 mM sodium nitrite to the solution, the results were nearly identical to the solution with no sodium nitrite at temperatures of 20 °C and beyond. Only at low temperatures did the trends change, and these changes were slight. At -4 °C the peak decreased to 16%, while at 5 °C the peak decreased to 54%, followed by flat behavior, which did not occur in the solution without sodium nitrite. These trends can be seen in Figure 37.

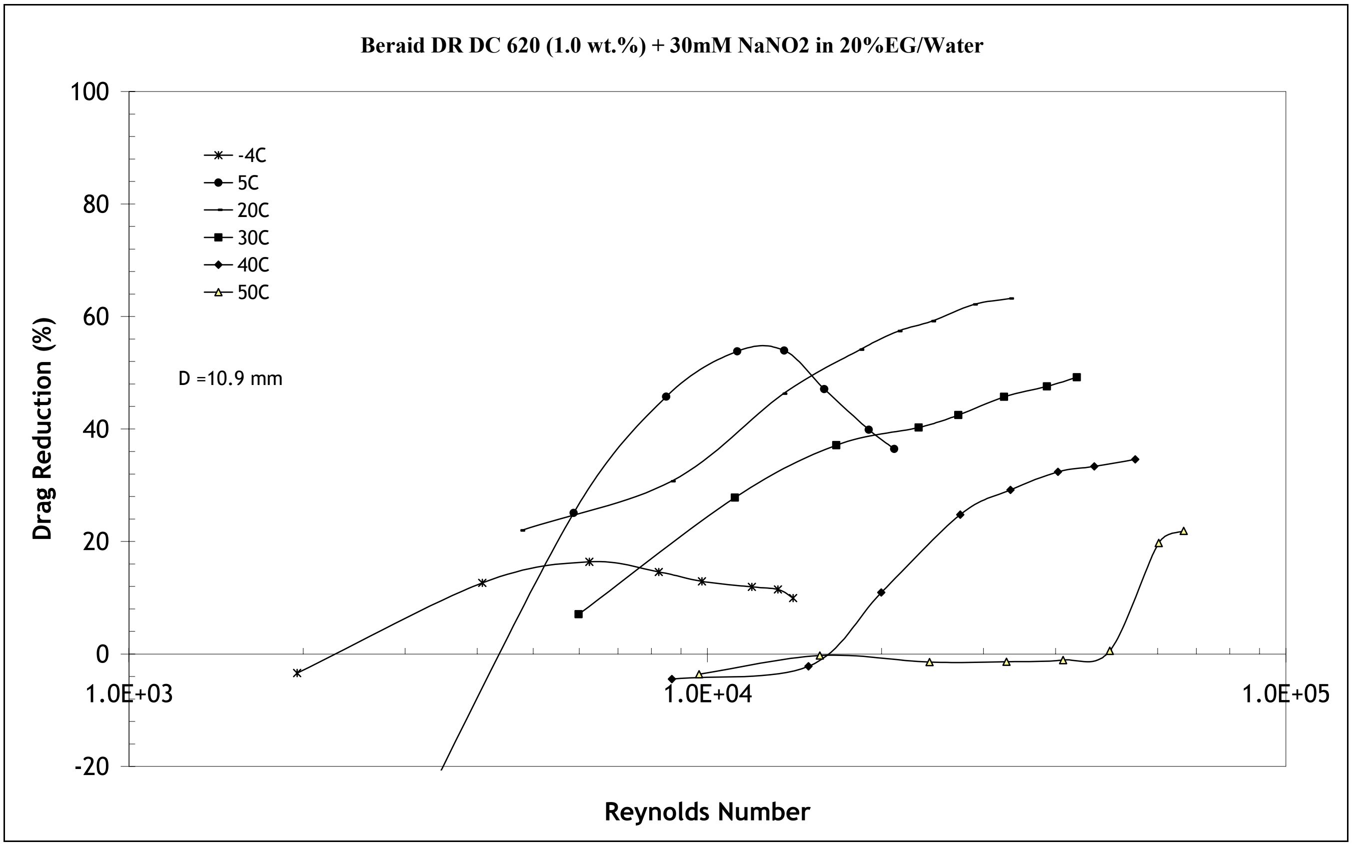


Figure 37: Beraid DR DC 620 (1.0 wt.%) + NaNO2 (30 mM) in 20% Ethylene Glycol/Water

3) <u>30% Glycerol/Water</u>

Another solvent in which Beraid DR DC 620 was tested at 1.0 wt.% concentration was 30% glycerol/water. The drag reducing behavior was very good, with a significant drag reduction temperature range of -4 to 30 °C. The peak at -4 °C was 50% drag reduction, after which the peak dropped off. For higher temperatures, the peaks did not drop off, and at 5, 20, and 30 °C the peaks were 75%, 70%, and 59%, respectively. The trends can be seen in Figure 38.

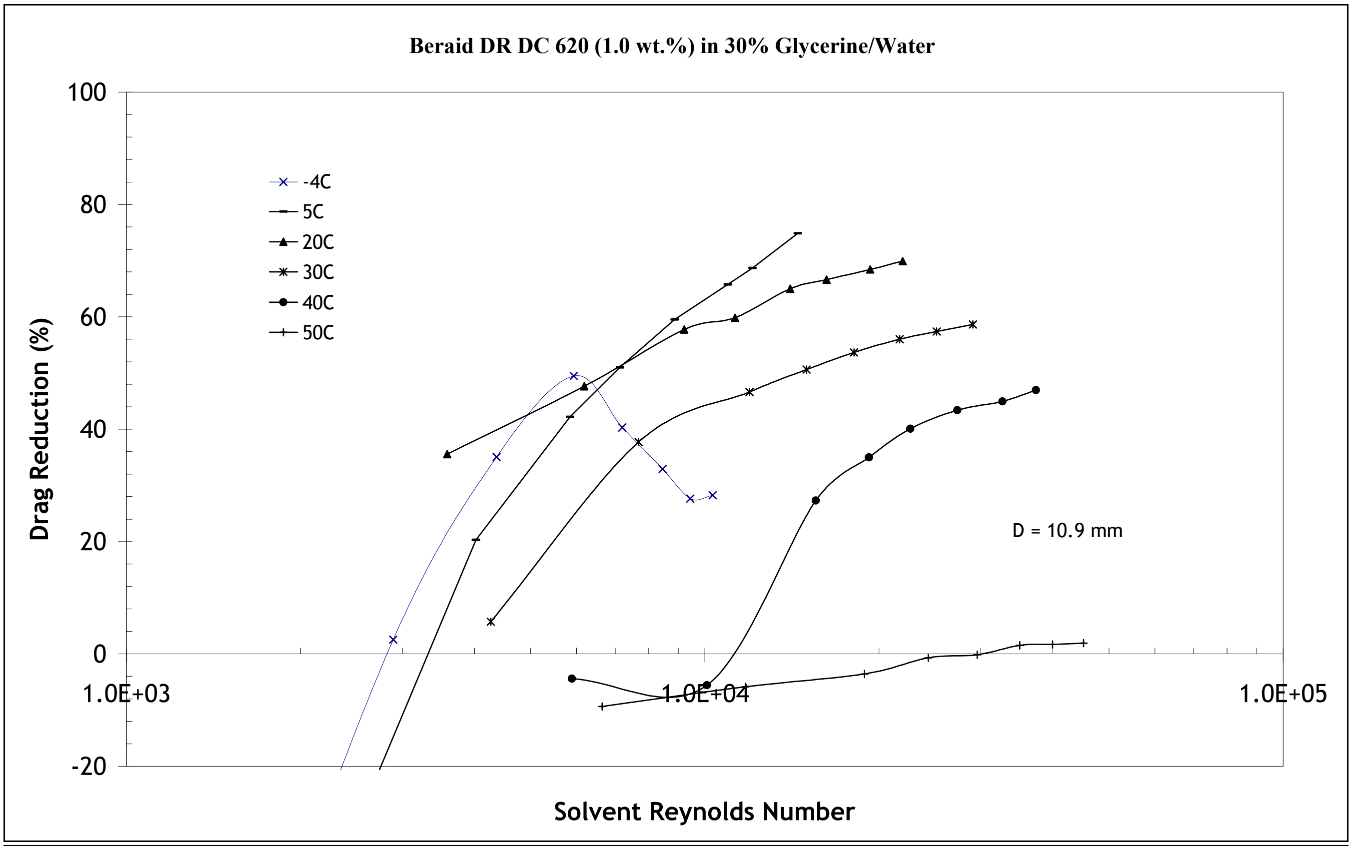


Figure 38: Beraid DR DC 620 (1.0 wt.%) in 30% Glycerol/Water

Once again, with the addition of sodium nitrite (30 mM), the drag reducing behavior did not change. This can be seen in Figure 39.

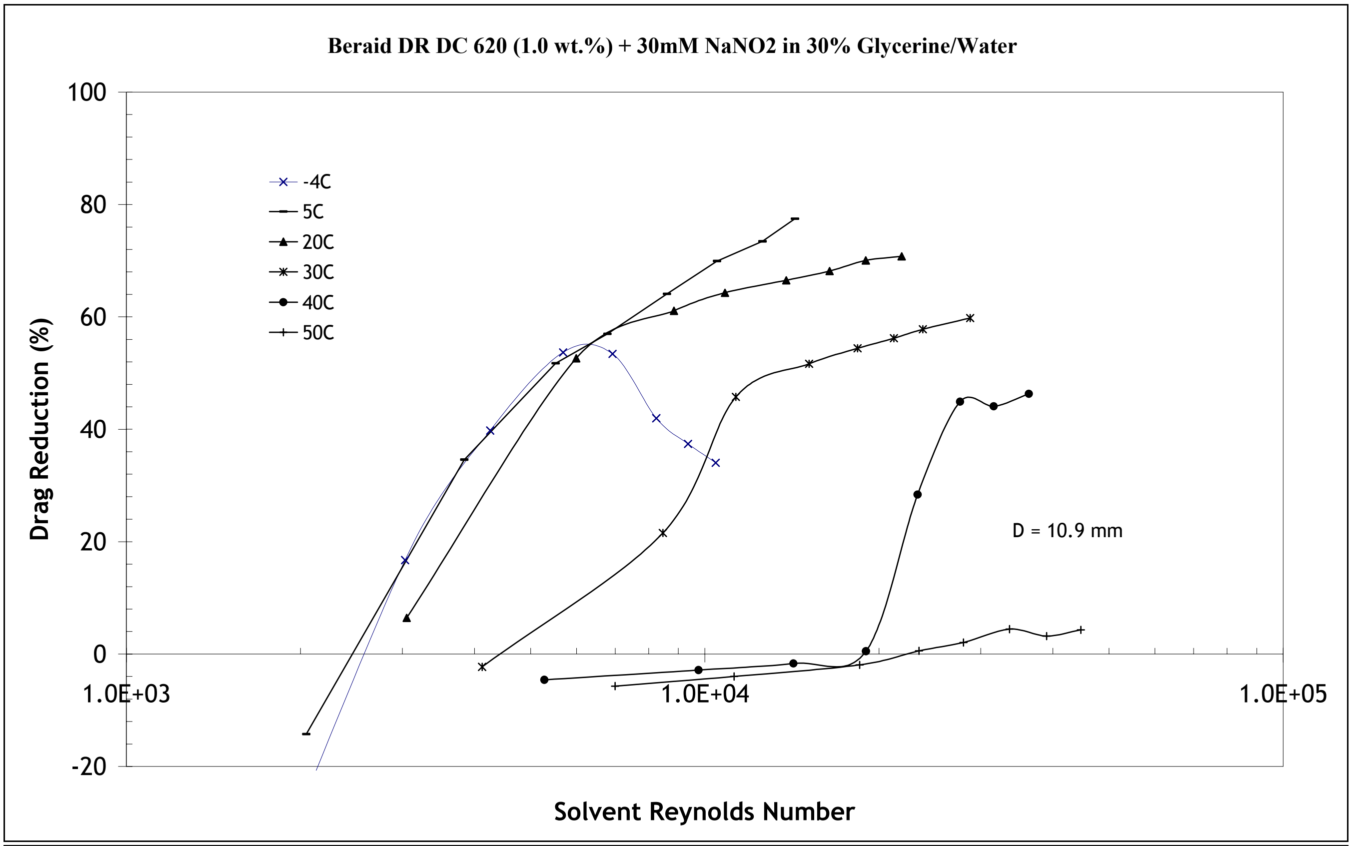


Figure 39: Beraid DR DC 620 (1.0 wt.%) + NaNO2 (30 mM) in 30% Glycerol/Water

4) <u>25% Propylene Glycol/Water</u>

The surfactant was tested at the same concentration (1.0 wt.%) in 25% propylene glycol/water, and showed no significant drag reducing behavior at any temperatures. Addition of 30 mM sodium nitrite had no effect on the observed drag reduction. These plots are included in Appendix B.

5) <u>Beraid DR DC 620 Summary</u>

A summary of the Beraid DR DC 620 results can be seen in Table 5, with the significant drag reduction temperature ranges listed. Also, the maximum drag reduction peaks are specified at 20 °C and at low temperatures. It should be noted that sodium nitrite does not have an effect on the drag reducing behavior of these solutions. Overall, Beraid DR DC 620 performed best for low temperature drag reduction in 30% glycerol/water, while for slightly higher temperature drag reduction, water was the best solvent.

Table 5: Summary of Beraid DR DC 620 Results

Surfactant	Surfactant Concentration (wt.%)	$NaNO_2$ (mM)	Solvent	Significant DR (>50%) Temperature Range (°C)	Maximum %DR (20 °C)	Maximum %DR (Low Temperature)
Beraid DR DC 620	1.0	0	Water	5 - 40	70%	58% (5°C)
Beraid DR DC 620	1.0	30	Water	5 - 40	71%	50% (5°C)
Beraid DR DC 620	1.0	0	20% EG/Water	5 - 20	62%	59% (5°C); 30% (-4°C)
Beraid DR DC 620	1.0	30	20% EG/Water	5 - 20	63%	54% (5°C); 16% (-4°C)
Beraid DR DC 620	1.0	0	30% Gly/Water	-4 - 30	70%	75% (5°C); 50% (-4°C)
Beraid DR DC 620	1.0	30	30% Gly/Water	-4 - 30	71%	77% (5°C); 54% (-4°C)
Beraid DR DC 620	1.0	0	25% PG/Water	No DR	-	-
Beraid DR DC 620	1.0	30	25% PG/Water	No DR	-	-

E) Chemoxide OL

Chemoxide OL is a commercial zwitterionic surfactant manufactured by Chemron. Its structure can be seen in Figure 40. The two experiments run with this surfactant had additions of sodium nitrite involved.

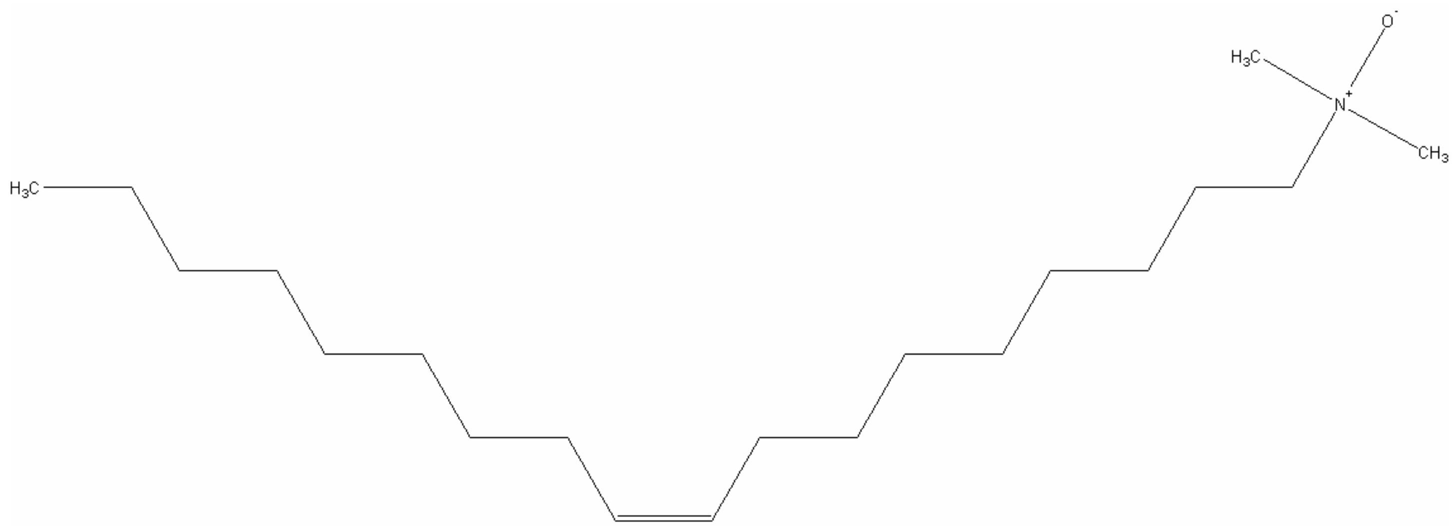


Figure 40: Chemoxide OL Structure

The first solution tested was 5 mM Chemoxide and sodium nitrite (30 mM) in 20% ethylene glycol/water. It exhibited significant drag reduction in the temperature range of 5 to 40 °C. The peaks at temperatures of 5 to 20 °C were broad but eventually dropped off at high Reynolds numbers, while the peaks at higher temperatures (40 °C) never dropped off. All the significant peaks were in the range of 50 to 60%. The trends can be seen in Figure 41.

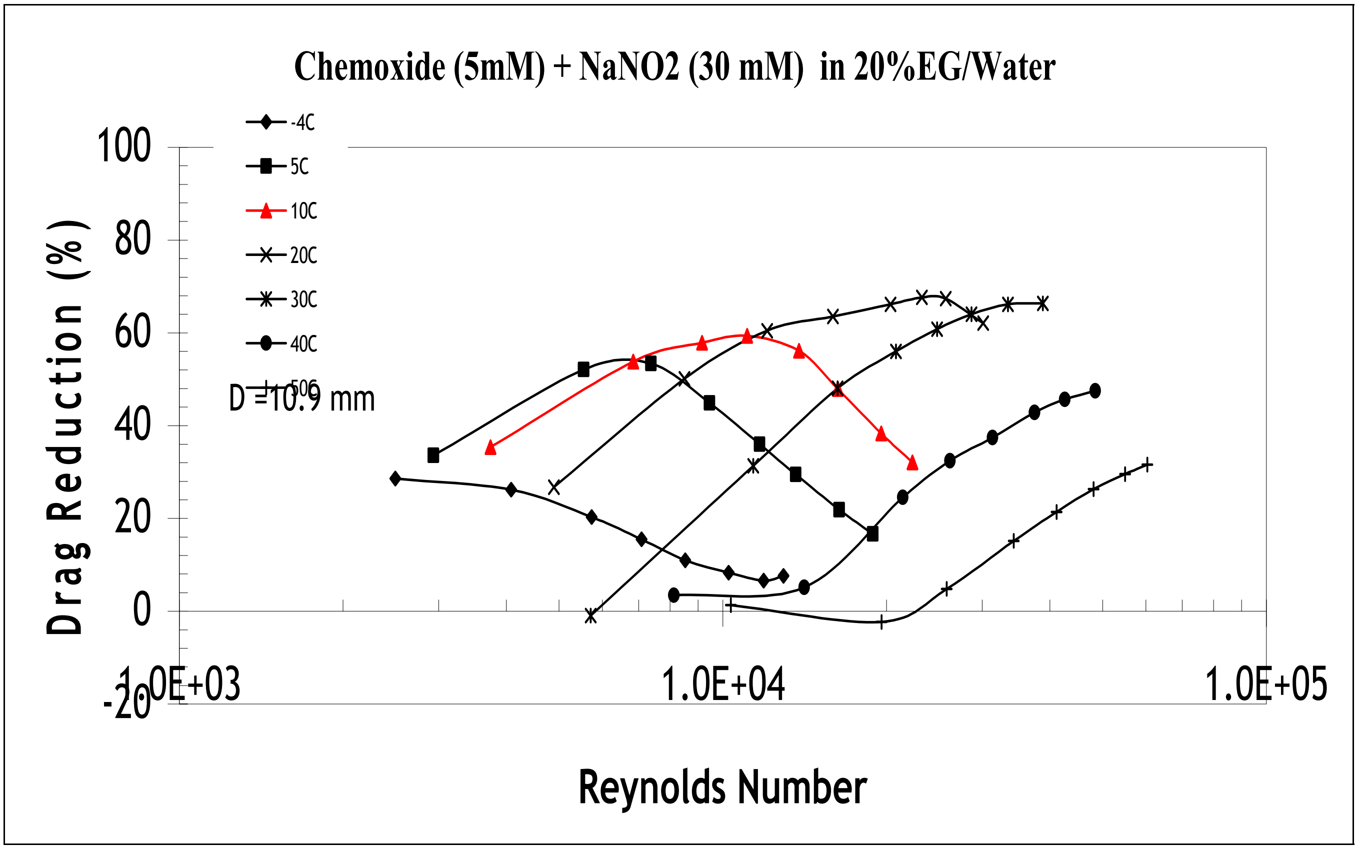


Figure 41: Chemoxide (5 mM) + NaNO2 (30 mM) in 20% Ethylene Glycol/Water

The other solution tested was 5 mM Chemoxide with 20 mM sodium nitrite in 30% glycerol/water. This solution exhibited significant drag reduction behavior in the temperature range of 10 to 50°C. Peaks in the 20 to 40 °C range reached up to 80% drag reduction. The peaks at temperatures of 30 to 50 °C never dropped off in the Reynolds number range tested, while at lower temperatures they did. The 10 °C peak reached a high of around 70% drag reduction. The trends can be seen in Figure 42. With the significant drag reduction behavior observed with sodium nitrite added in both 20% ethylene glycol/water and 30% glycerol/water solutions, further testing of these solutions should be performed.

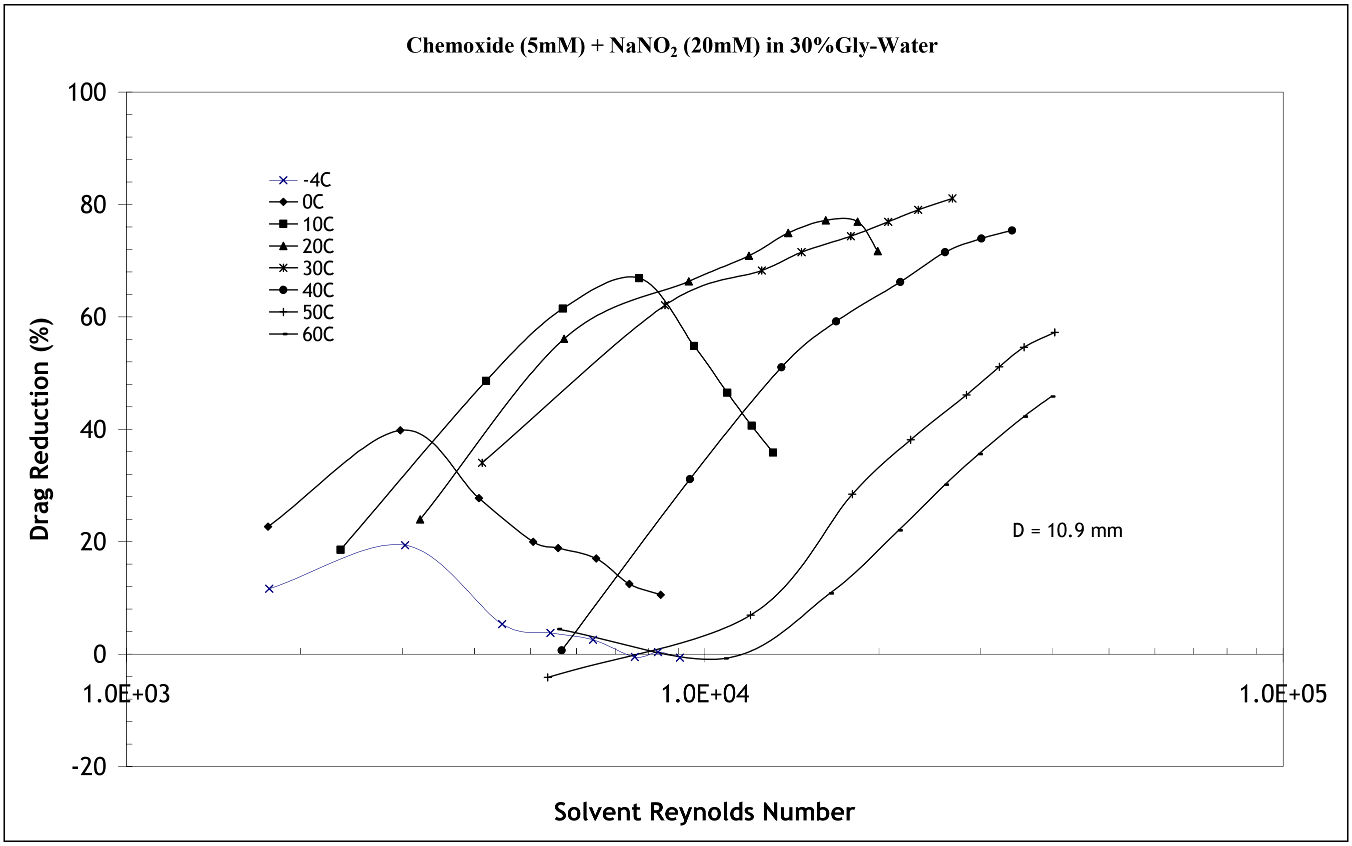


Figure 42: Chemoxide (5 mM) + NaNO2 (20 mM) in 30% Glycerol/Water

F) Oleyl Betaine

Oleyl Betaine is a zwitterionic surfactant synthesized by Dr. Hart and Dr. Oba. Its structure can be seen in Figure 43.

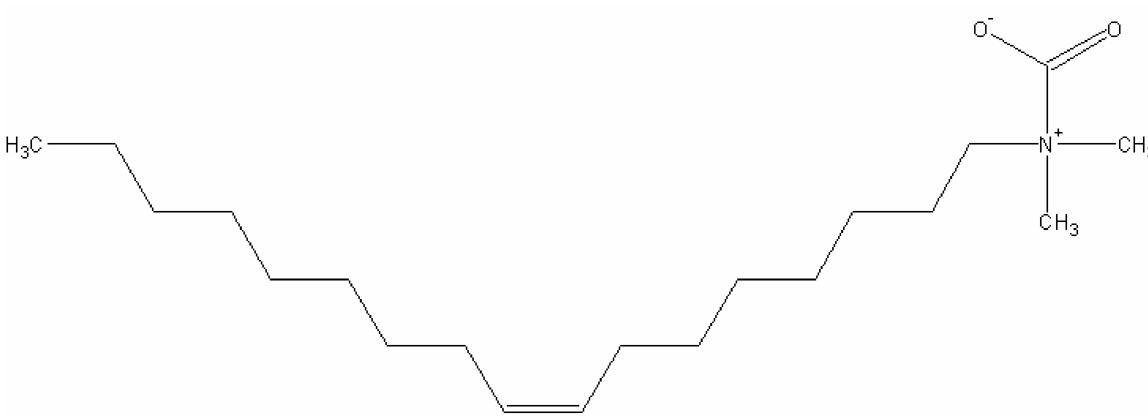


Figure 43: Oleyl Betaine Structure

The solutions tested all contained the zwitterionic Oleyl Betaine with an anionic additive in a 4:1 ratio (4.8 mM: 1.2 mM). Sodium Dodecyl Sulfate (SDS) and Sodium Dodecyl Benzenesulphonate (SDBS) were the anionic surfactant additives. There structures can be seen in Figures 44 and 45.

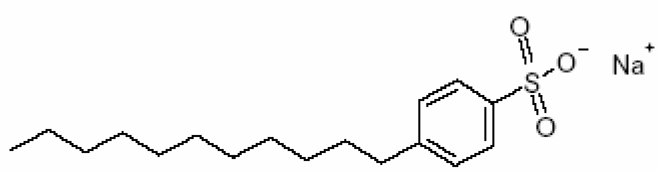


Figure 44: SDBS Structure

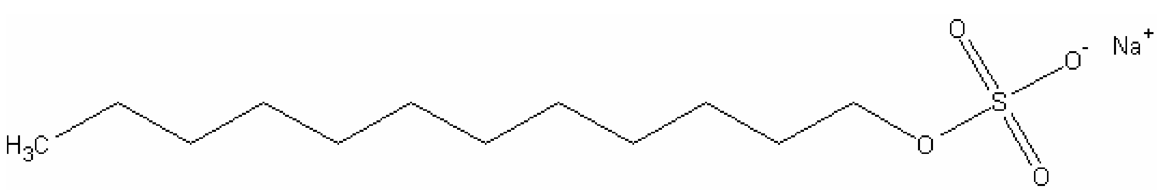


Figure 45: SDS Structure

The first solution tested was oleyl betaine (4.8 mM) and SDBS (1.2 mM) in 20% ethylene glycol/water. No drag reduction was observed. Oleyl betaine (4.8 mM) and SDS (1.2 mM) were tested in two solvents, water and 20% ethylene glycol/water, and no drag reduction was observed in either solution. The plots for these three solutions can be found in Appendix C.

G) Oleyl (Chem) Betaine

Oleyl (chem) betaine is a commercial zwitterionic surfactant manufactured by Chemron. It has the same structure as the surfactant synthesized by Dr. Hart, which can be seen in Figure 46. Despite the poor results with the synthesized oleyl betaine, it was thought that perhaps the commercial surfactant would perform better.

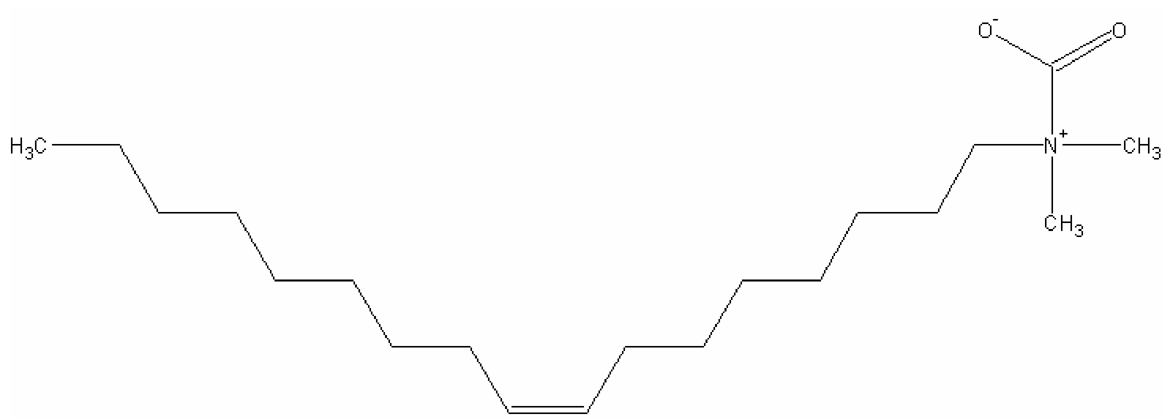


Figure 46: Oleyl (Chem) Betaine Structure

This surfactant was tested in combination with sodium dodecyl benzenesulphonate (SDBS), an anionic surfactant, in a 4:1 (4.8mM:1.2 mM) ratio of zwitterionic to anionic surfactant. The structure of SDBS can be seen in Figure 44.

This combination was first tested in water with various concentrations (0, 6, 12, 20, and 30 mM) of sodium nitrite. No significant drag reduction was observed for any of these solutions, and the results were consistent at all temperatures tested (10 – 60°C), with the drag reduction staying between 0 and 10%. These plots can be found in Appendix D. The surfactant combination was then tested in 20% ethylene glycol/water, with and without sodium nitrite (6 mM). Results were similar to those in water, with the drag reduction staying within 0 to 20% drag reduction at all temperatures. These plots can also be found in Appendix D. The 4:1 ratio of oleyl (chem) betaine to SDBS is not an effective drag reducing combination, and the addition of salt does not improve the drag reducing ability of these solutions.

H) N-7

N-7 is a non-ionic surfactant synthesized by Dr. Hart and Dr. Oba. It has the second longest overall chain of the surfactants tested. It is named N-7 because of the seven repeating ethoxy groups on the polar head end of the surfactant. The structure can be seen in Figure 47.

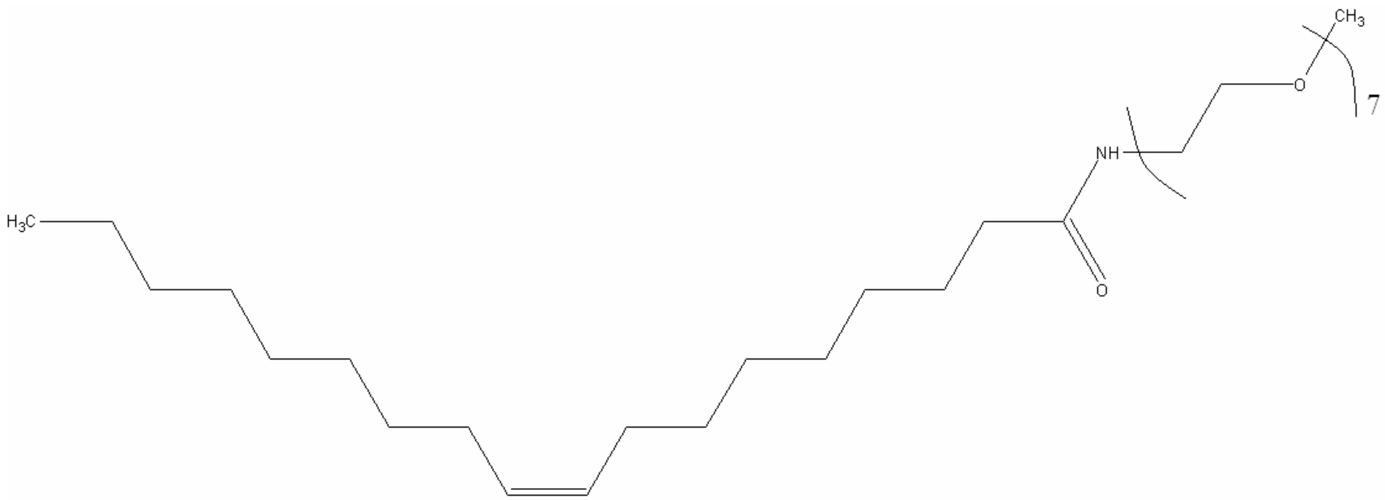


Figure 47: N-7 Structure

The sample of N-7 was the remainder of a sample synthesized by Dr. Hart and Dr. Oba. Therefore, only 0.5 wt.% N-7 was tested in water. Drag reduction was steady but low, between 5 and 20% at all temperatures (5 – 60 °C). This surfactant might be more promising if a higher concentration was used, and it therefore warrants further testing. Its plot can be found in Appendix E.

I) N-13

N-13 is another non-ionic surfactant synthesized by Dr. Hart and Dr. Oba. It contains the same structure except the ethoxy groups on the polar head end of the surfactant number 13 instead of 7. This structure can be seen in Figure 48.

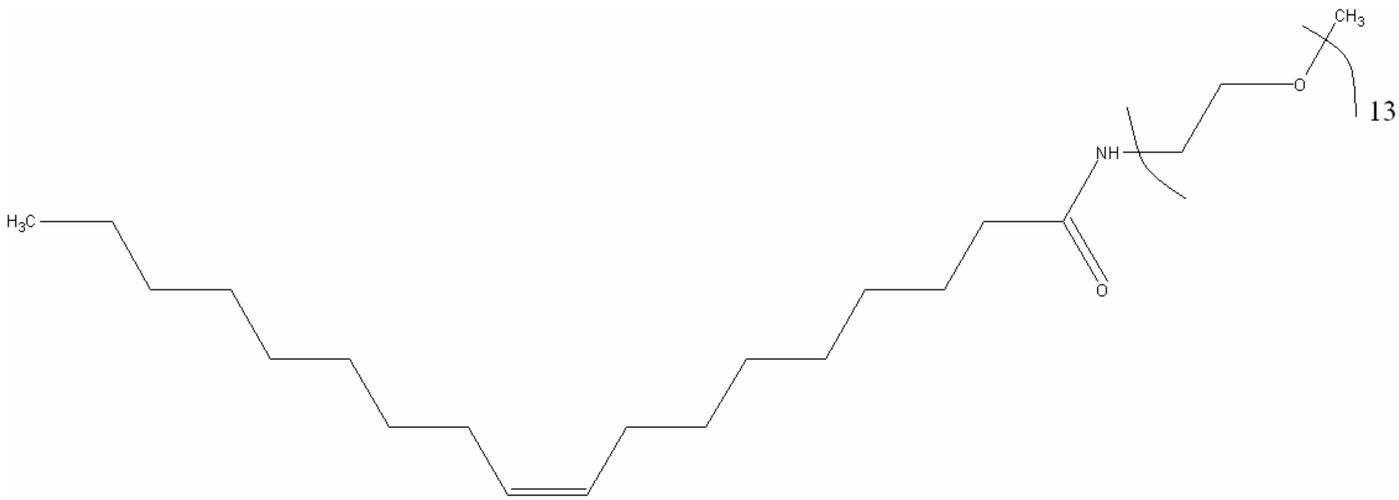


Figure 48: N-13 Structure

A new sample of the synthesized surfactant was used to add an additional 6.5 L of N-13 (5 mM) in water with sodium nitrite (5 mM) to an old solution containing this surfactant. No drag reduction was observed, and the addition of 25 mM more of sodium nitrite to give a solution containing 30 mM sodium nitrite did not exhibit any drag reduction either. These plots can be found in Appendix E. The lack of drag reduction might be attributed to the age and decay with time of the solution with which the new sample was combined, or, more likely, this surfactant may not exhibit significant drag reducing behavior.

Conclusions

A) It is feasible to use zwitterionic and non-ionic surfactants in district cooling systems. These surfactants are more biodegradable, which means that some of them may be more promising than less biodegradable cationic surfactants.

B) Oleyl Trimethylaminimide is a promising zwitterionic surfactant in both water and 20% ethylene glycol/water, with better drag reducing behavior for lower and higher temperatures in 20% ethylene glycol/water. A promising feature of this surfactant is its ability to exhibit drag reducing behavior at low concentrations (down to 200 ppm). Also, the addition of sodium nitrite to the oleyl trimethylaminimide solutions helps increase low temperature drag reduction behavior, although drag reduction performance at higher temperatures decreased with salt additions. Also, high concentrations of sodium nitrite (30 mM) are more inconsistent than and not as promising as smaller amounts of sodium nitrite. Overall, oleyl trimethylaminimide is a versatile surfactant in its ability to perform in a variety of concentrations and solutions with different concentrations of salt additives. Its drag reducing behavior should be explored further.

C) DR0206 has good drag reducing behavior in water at middle to high temperature ranges. With the addition of 30 mM sodium nitrite, especially high peaks (around 80%) were observed at higher temperatures (50 and 60 °C). In 20% ethylene glycol/water solutions no drag reduction ability was observed for this surfactant.

D) SPE98300 is a promising surfactant in the middle to high temperature range that has good drag reduction results with sodium nitrite additions. The best solvent for this surfactant is water, with the significant drag reduction temperature range being from 20 to 70 °C with 30 mM sodium nitrite. In 30% glycerol/water, the significant drag reduction temperature range was 20 to 50 °C with 30 mM sodium nitrite. In all solvents, the addition of sodium nitrite (30 mM) caused the significant drag reduction temperature ranges to increase, along with the peaks in these ranges.

E) Beraid DR DC 620 is a promising surfactant in the low to middle temperature range. The best solvent for this surfactant is 30% glycerol/water for low temperature drag reduction, while for high temperature drag reduction, water was the best solvent.

F) Oleyl Betaine, both the commercial surfactant (Oleyl (Chem)Betaine) manufactured by Chemron and a product synthesized by Dr. Hart and Dr. Oba, does not exhibit good drag-reducing behavior in a 4:1 molar ratio with an anionic additive such as sodium dodecyl sulfate (SDS) or sodium dodecyl benzenesulphonate (SDBS). The concentrations tested were 4.8 mM oleyl betaine to 1.2 mM of the anionic additive.

References

1) Bailey, Leslie. "Study of Drag Reduction By Surfactants in Low Temperature Ethylene Glycol/Water Systems." B.S. Honors Thesis, The Ohio State University, Columbus, 2004.

2) Gasljevic, K. and Matthys, E.F. "Field Demonstration of Pumping Power Reduction in a Hydronic HVAC System with Drag-Reducing Surfactant Additives." ASME International Mechanical Engineering Congress and RD&D Expo, 2004.

3) Harwigsson, Ian, Fredrik, Tiberg, and Chevalier, Yves. "Nature of the Adsorption of Zwitterionic Surfactants at Hydrophilic Surfaces." *Journal of Colloid and Interface Science*. 183 (1996) 380-387.

4) Hellsten, Martin and Harwigsson, Ian. "Use of a Betaine Surfactant Together with an Anionic Surfactant as a Drag-Reducing Agent." PCT International Application (1996).

5) Michels, B. and Waton, G. "Kinetics Associated with the Length Change of Micelles in SDS Solutions." *Journal of Physical Chemistry*. B (2000), 104, 228-232

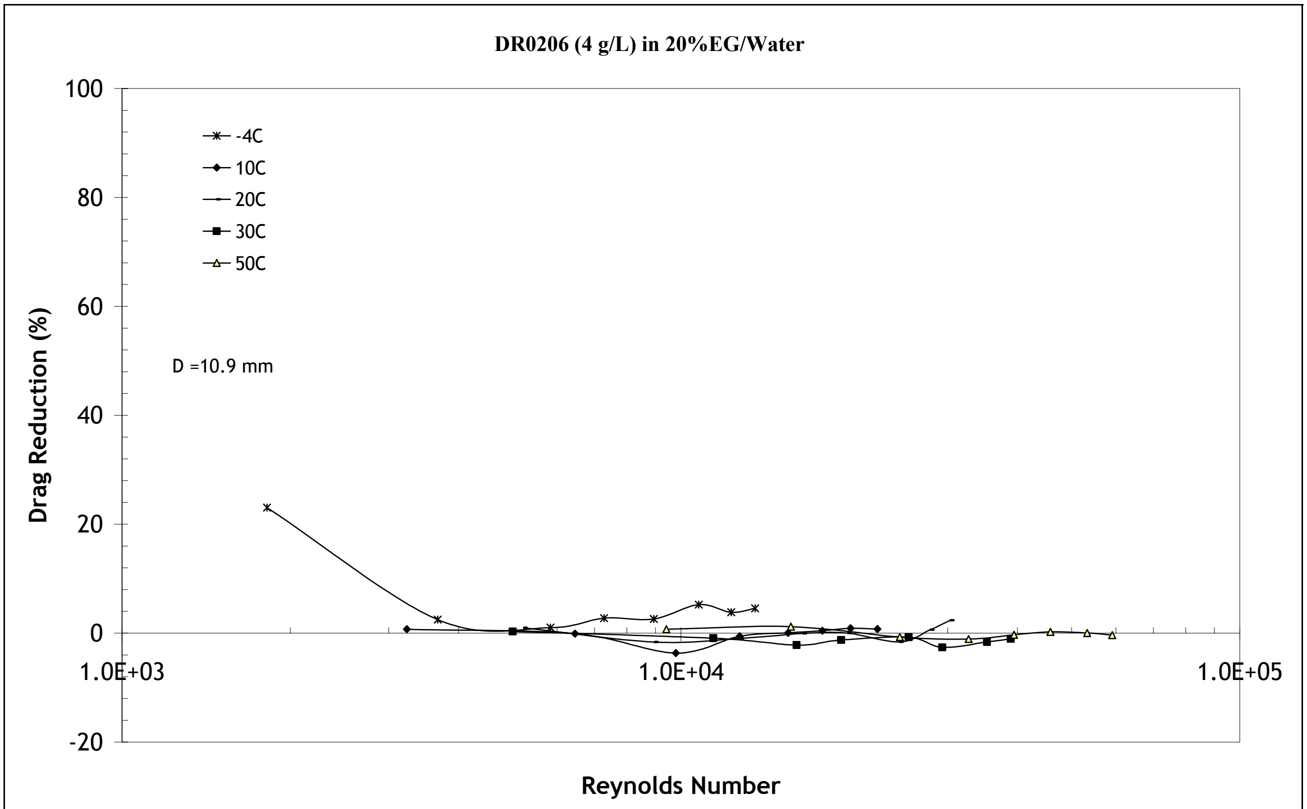
6) Miller, Megan. "Low Temperature Drag Reduction of Non-ionic and Zwitterionic Surfactants." B.S. Honors Thesis, The Ohio State University, Columbus, 2004.

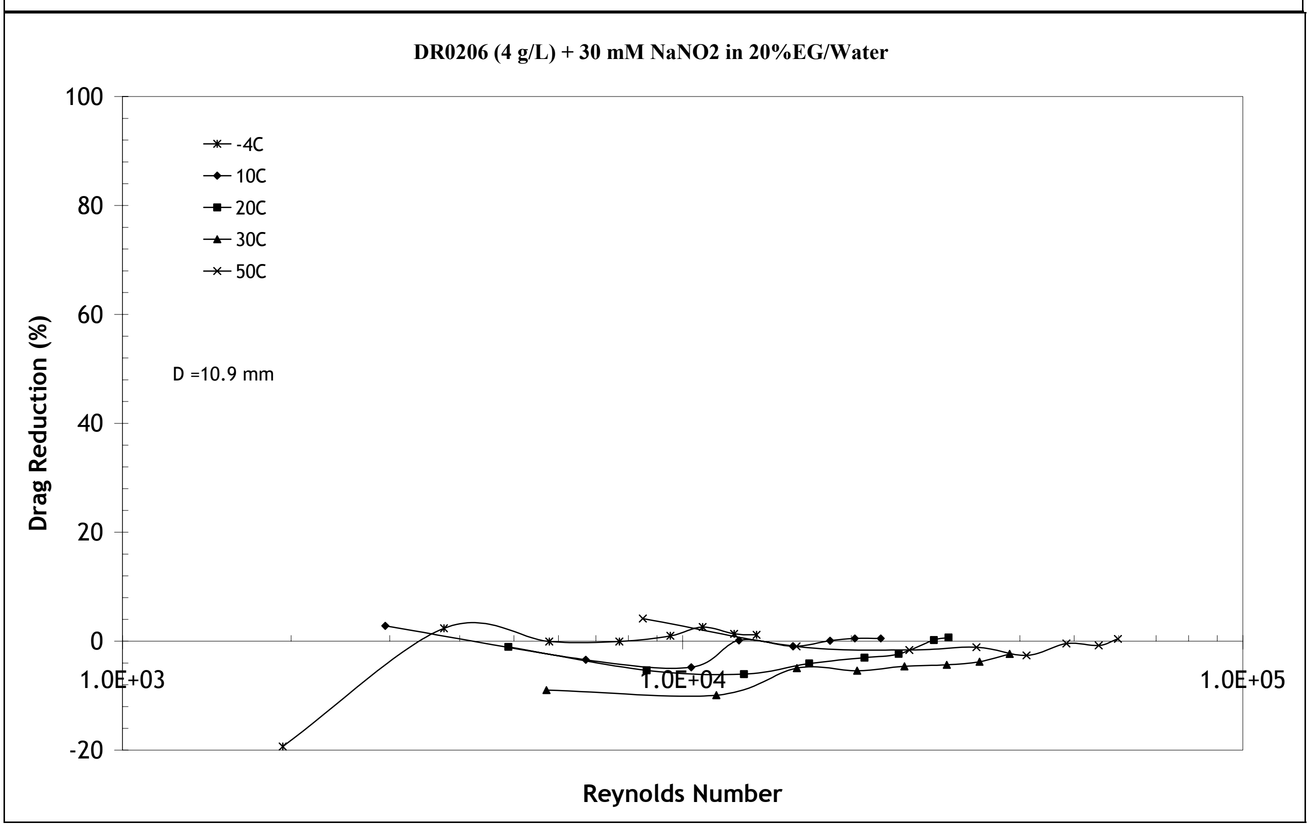
7) Missel. P.J., N.A. Mazer, G.B. Benedek and M.C. Carey, *Journal of Physical Chemistry*. 84 (1980), 1044-1057.

8) Myska, Jiri et. al. "Influence of salts on dynamic properties of drag reducing surfactants." *Journal of Non-Newtonian Fluid Mechanics*. 97 (2001) 251-266.

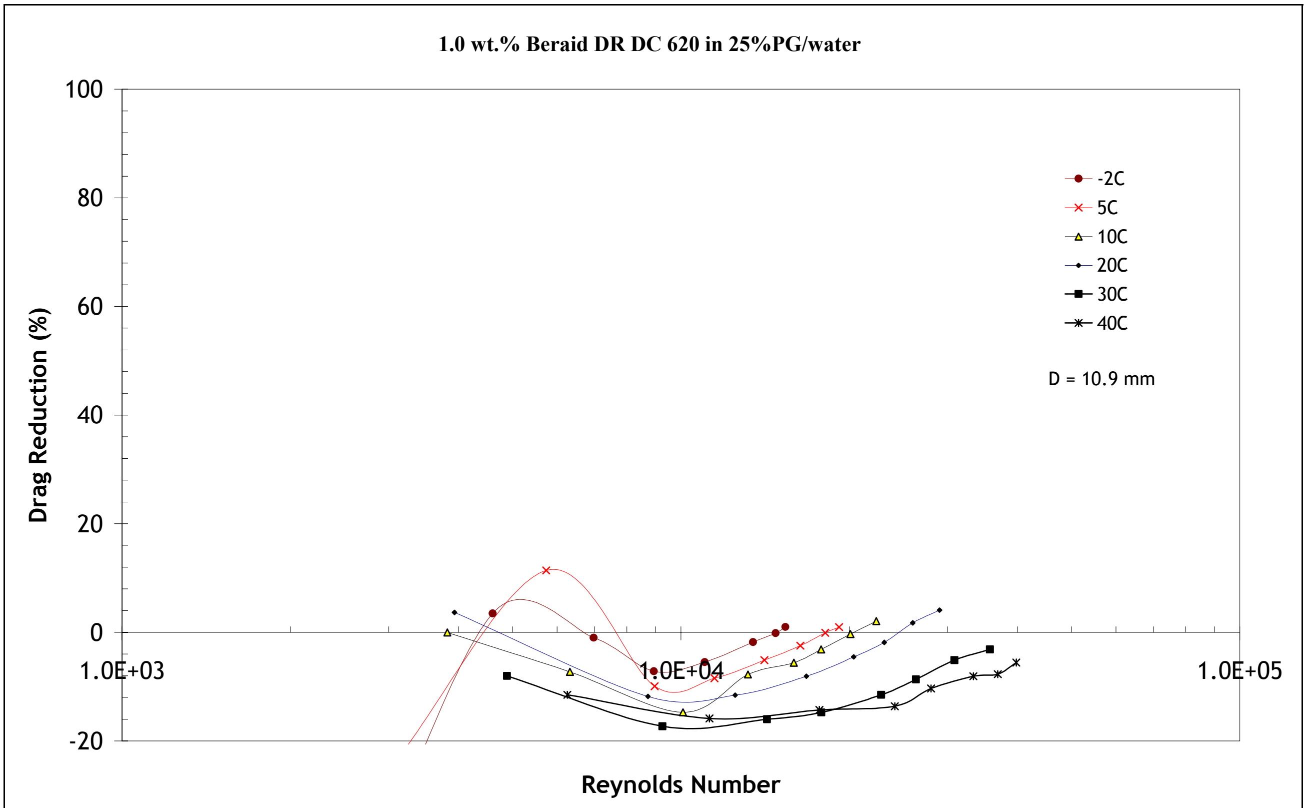
9) Zakin, J. L., Lu B., and Bewersdorff, H. W. "Surfactant Drag Reduction." *Reviews in Chemical Engineering*, 13 (4-5), (1998) 253-320.

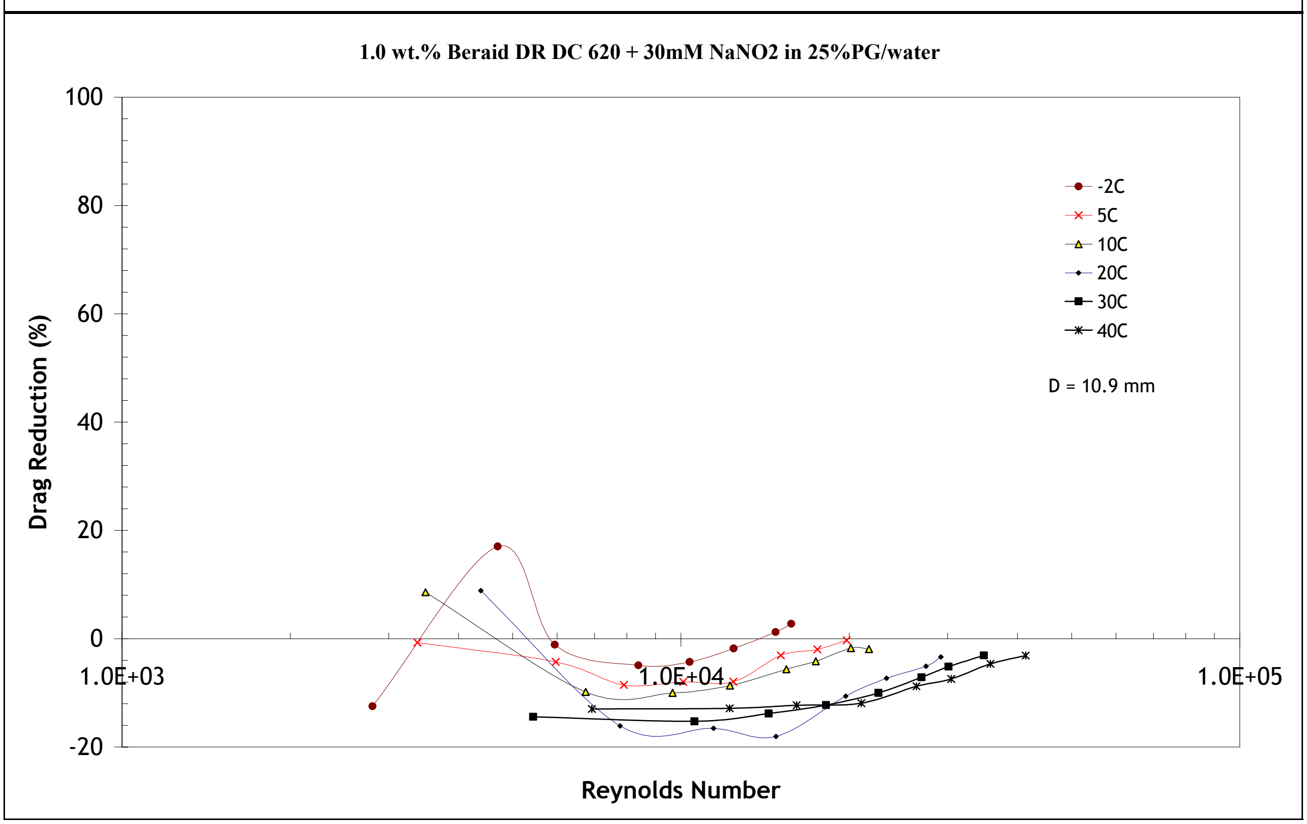
APPENDIX A


DR0206 (4 g/L) in 20%EG/Water
100
80
60
40
20
0
-20
Drag Reduction (%)
-4C
10C
20C
30C
50C
D =10.9 mm
1.0E+03
1.0E+04
1.0E+05
Reynolds Number

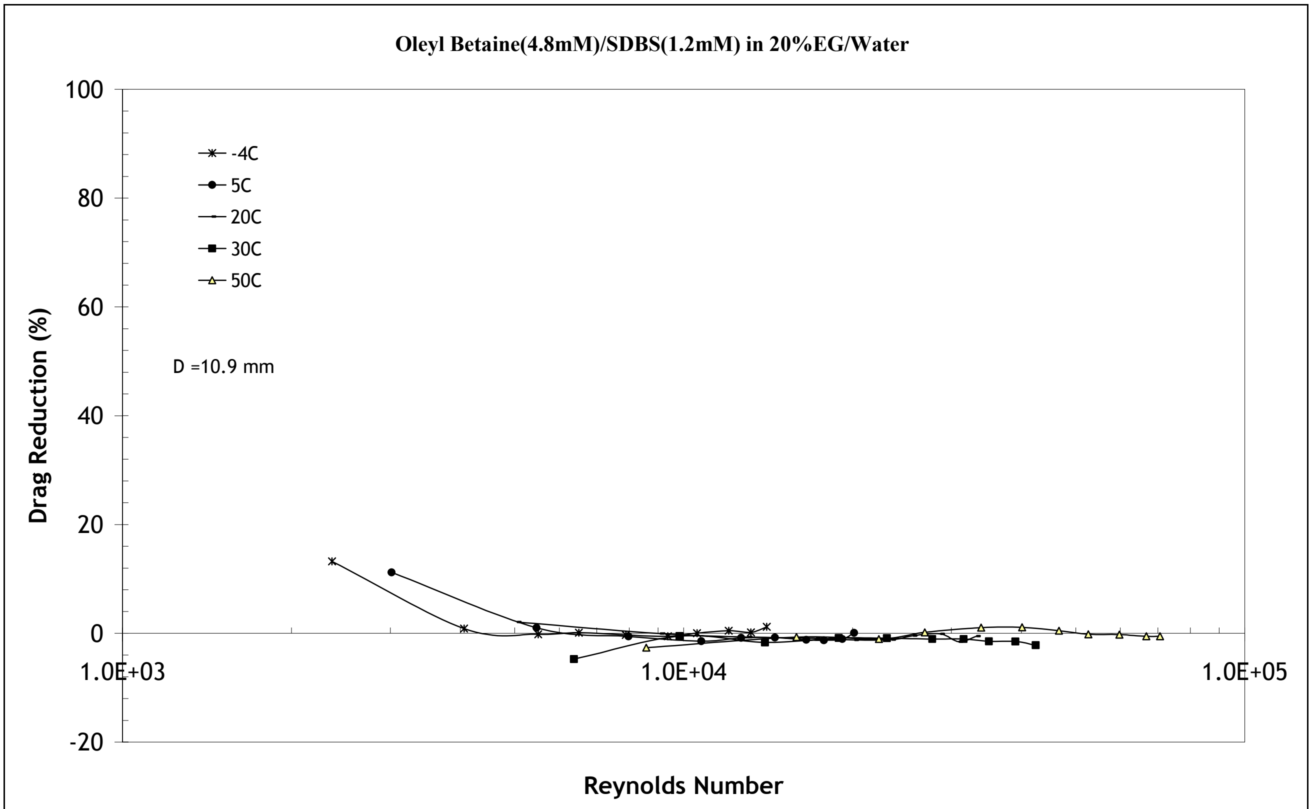

DR0206 (4 g/L) + 30 mM NaNO2 in 20%EG/Water
100
80
60
40
20
0
-20
Drag Reduction (%)
-4C
10C
20C
30C
50C
D =10.9 mm
1.0E+03
1.0E+04
1.0E+05
Reynolds Number

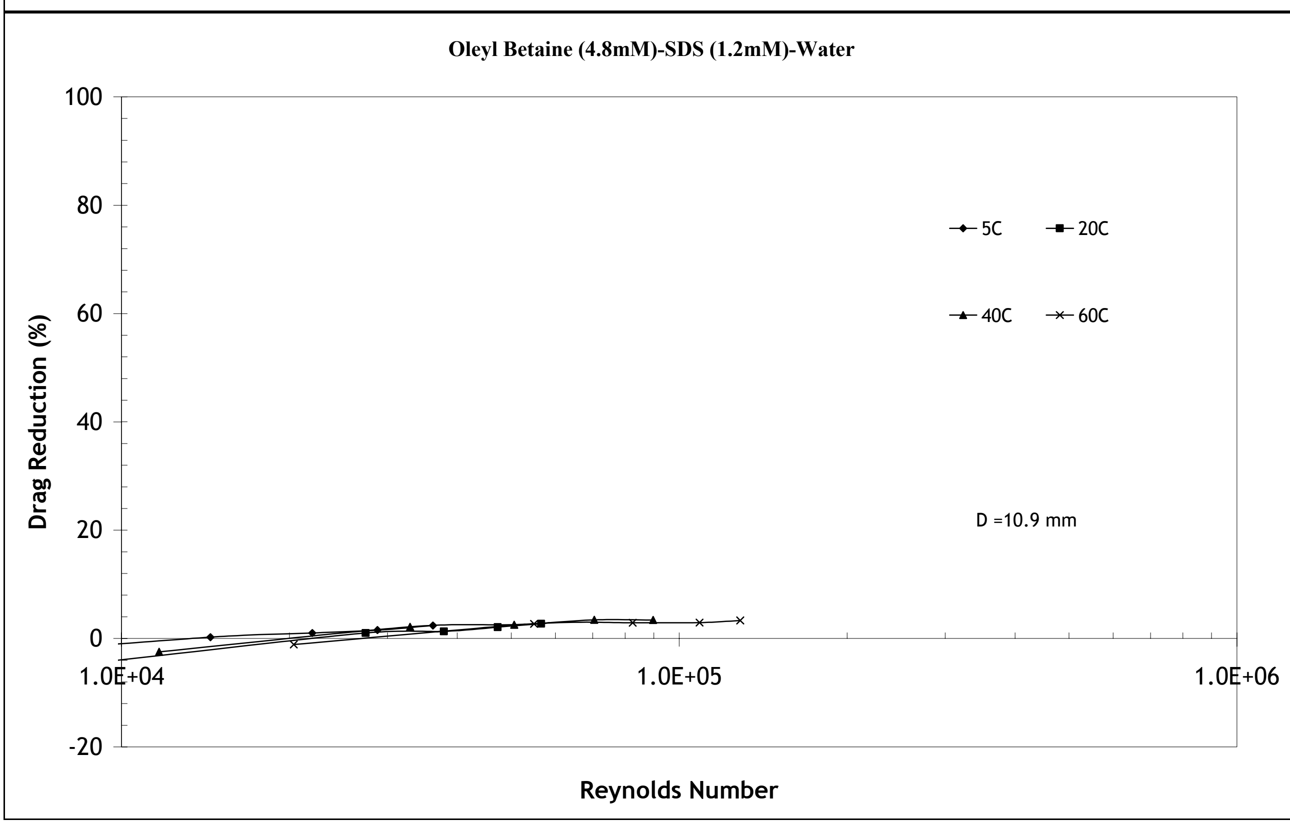
APPENDIX B

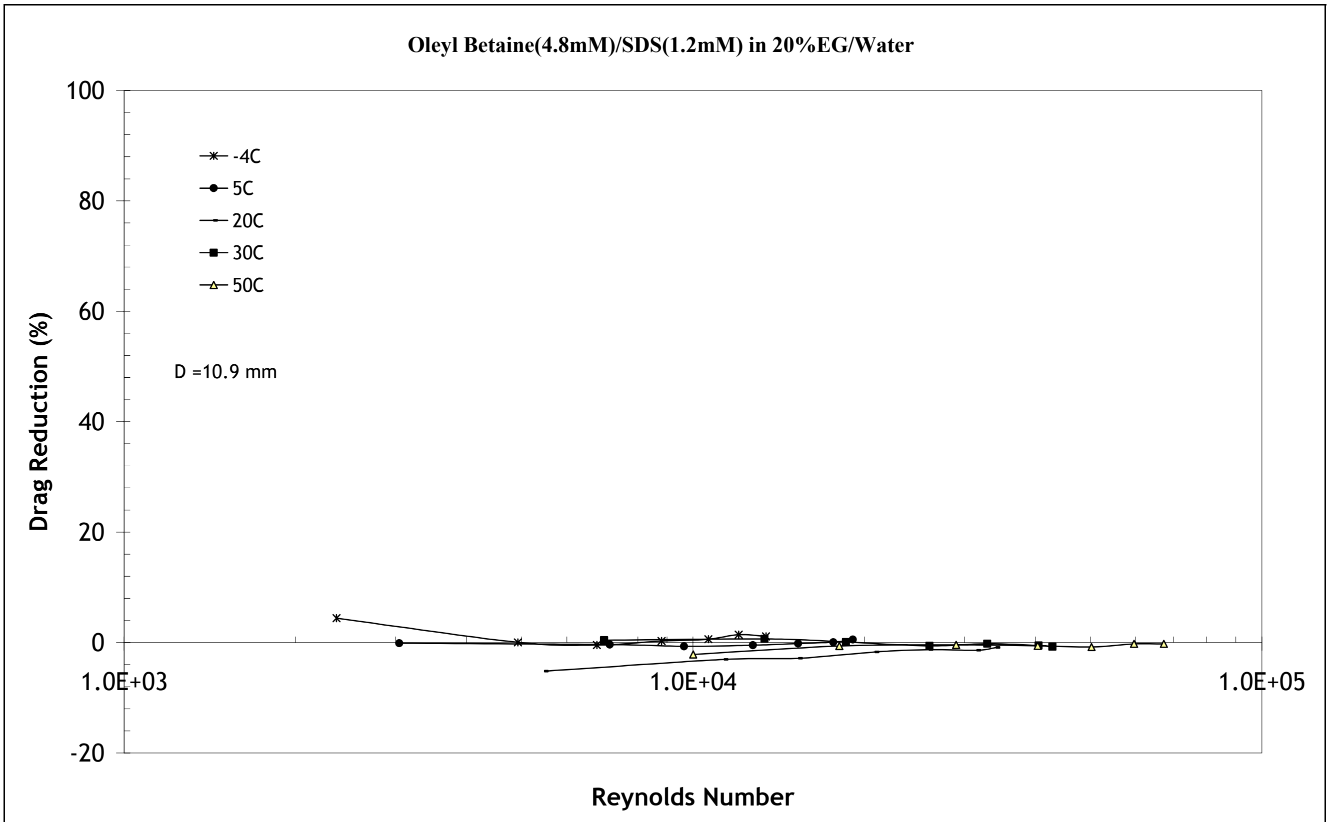

1.0 wt.% Beraid DR DC 620 in 25%PG/water
Drag Reduction (%)
Reynolds Number
100
80
60
40
20
0
-20
1.0E+03
1.0E+04
1.0E+05
-2C
5C
10C
20C
30C
40C
D = 10.9 mm

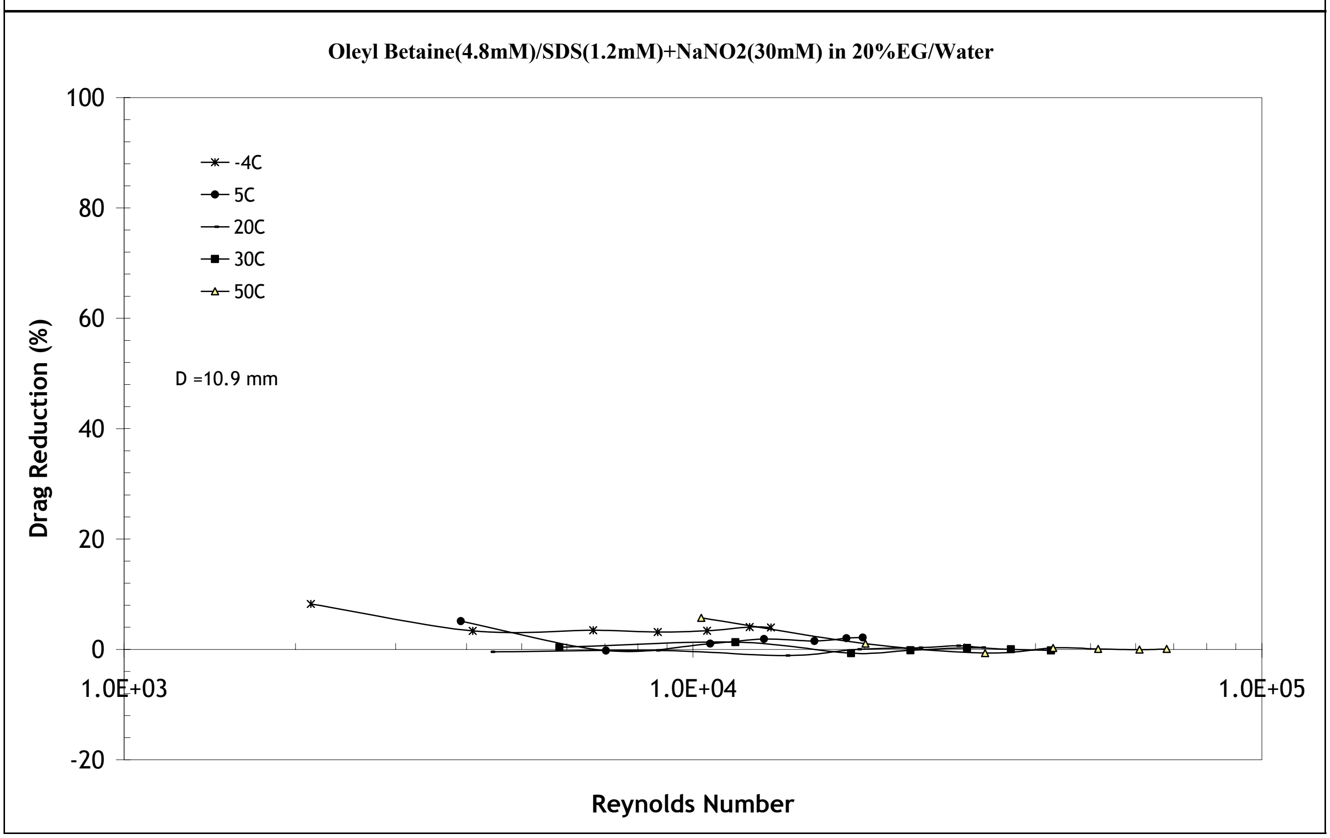

1.0 wt.% Beraid DR DC 620 + 30mM NaNO2 in 25%PG/water
Drag Reduction (%)
Reynolds Number
100
80
60
40
20
0
-20
1.0E+03
1.0E+04
1.0E+05
-2C
5C
10C
20C
30C
40C
D = 10.9 mm

APPENDIX C

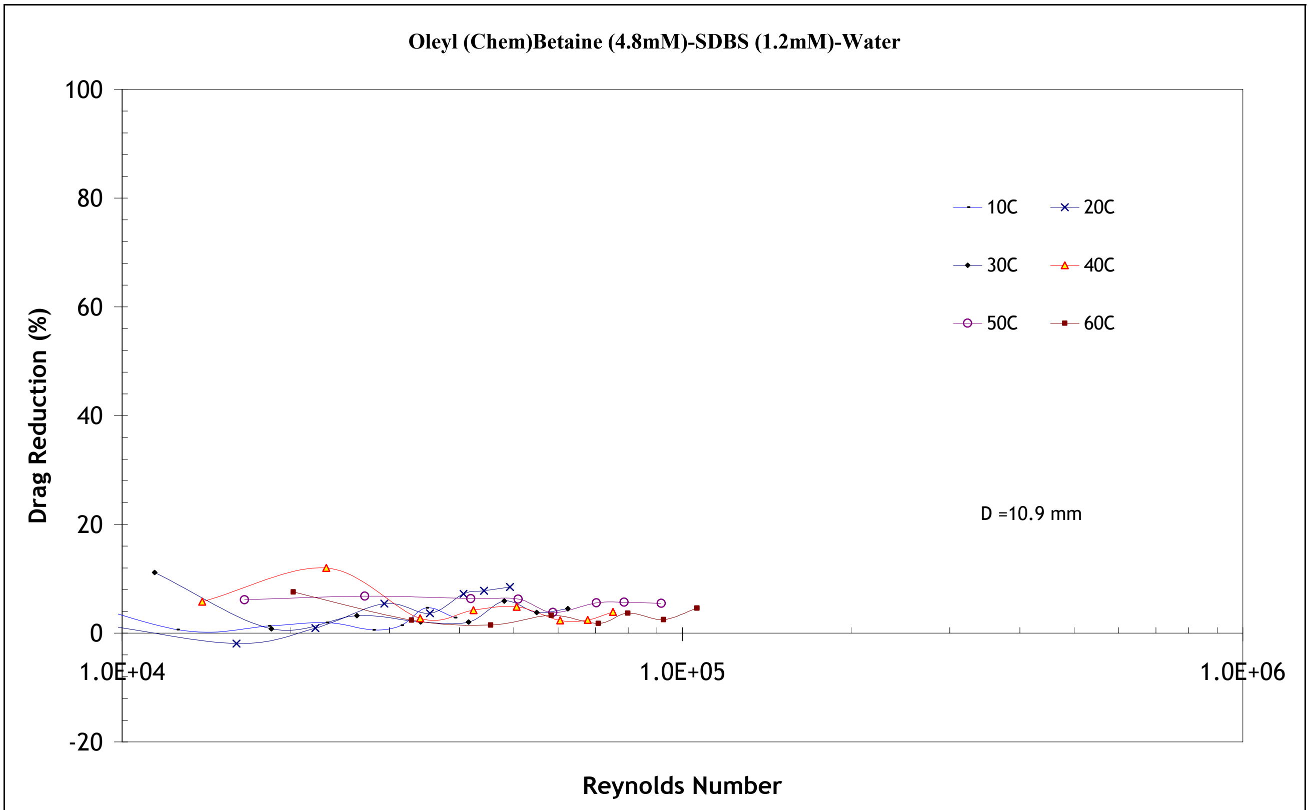

Oleyl Betaine(4.8mM)/SDBS(1.2mM) in 20%EG/Water
100
80
60
40
20
0
-20
1.0E+03
1.0E+04
1.0E+05
-4C
5C
20C
30C
50C
D =10.9 mm
Drag Reduction (%)
Reynolds Number

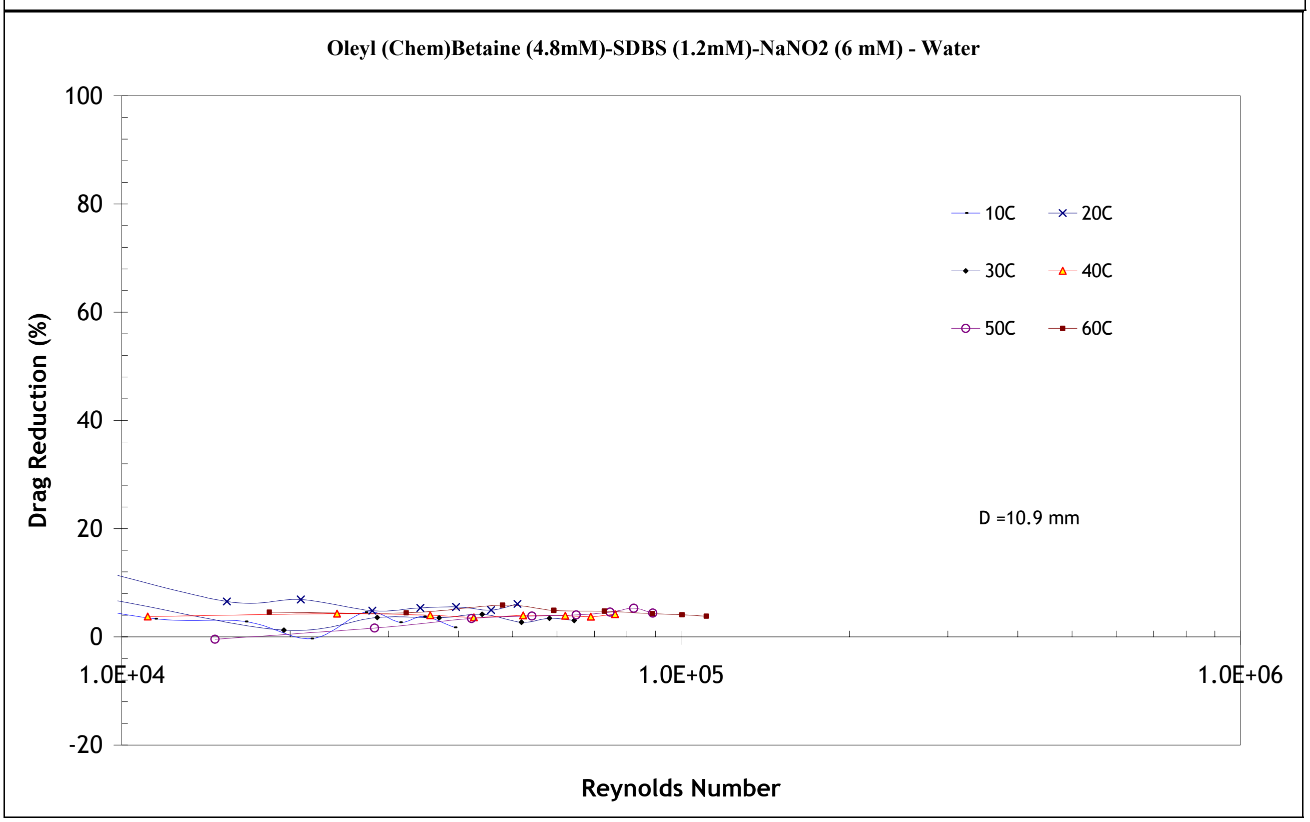

Oleyl Betaine (4.8mM)-SDS (1.2mM)-Water
100
80
60
40
20
0
-20
1.0E+04
1.0E+05
1.0E+06
5C
20C
40C
60C
D =10.9 mm
Drag Reduction (%)
Reynolds Number

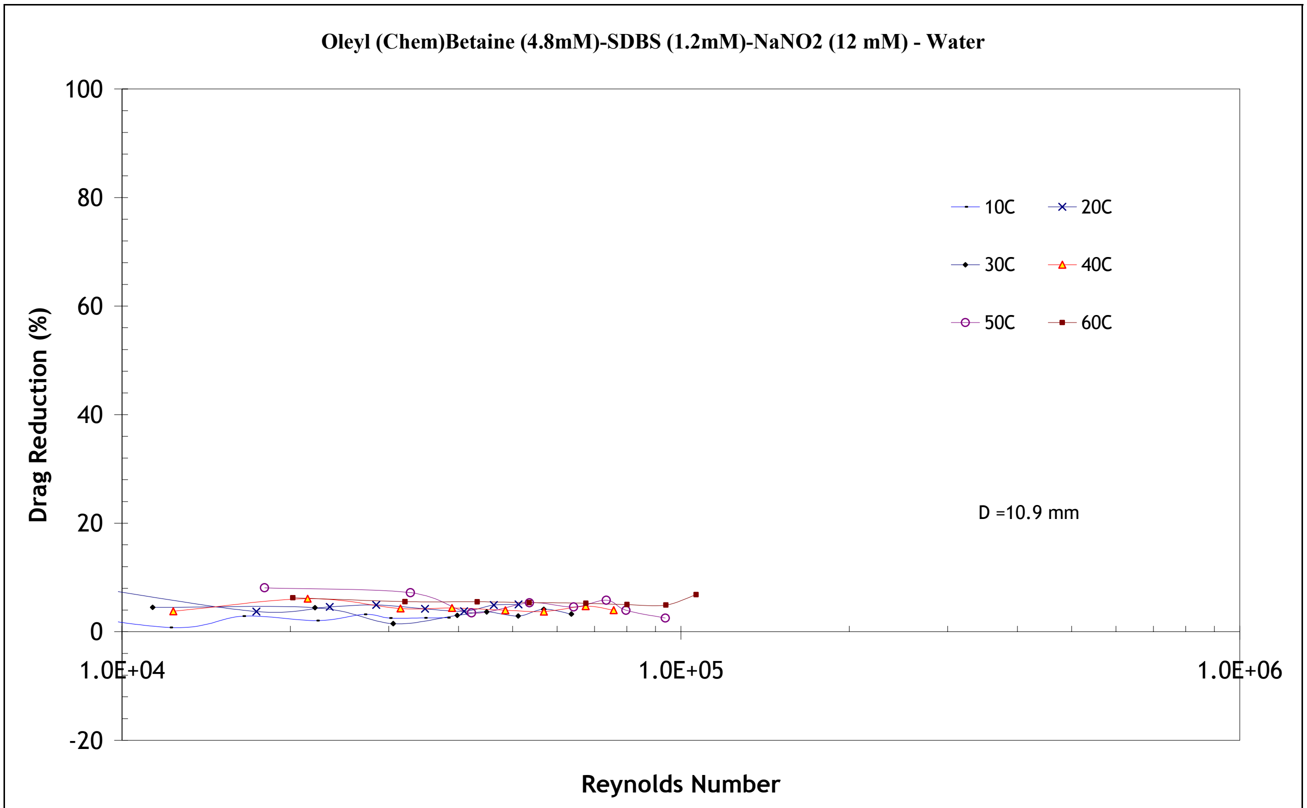

Oleyl Betaine(4.8mM)/SDS(1.2mM) in 20%EG/Water
Drag Reduction (%)
Reynolds Number
-4C
5C
20C
30C
50C
D =10.9 mm
100
80
60
40
20
0
-20
1.0E+03
1.0E+04
1.0E+05

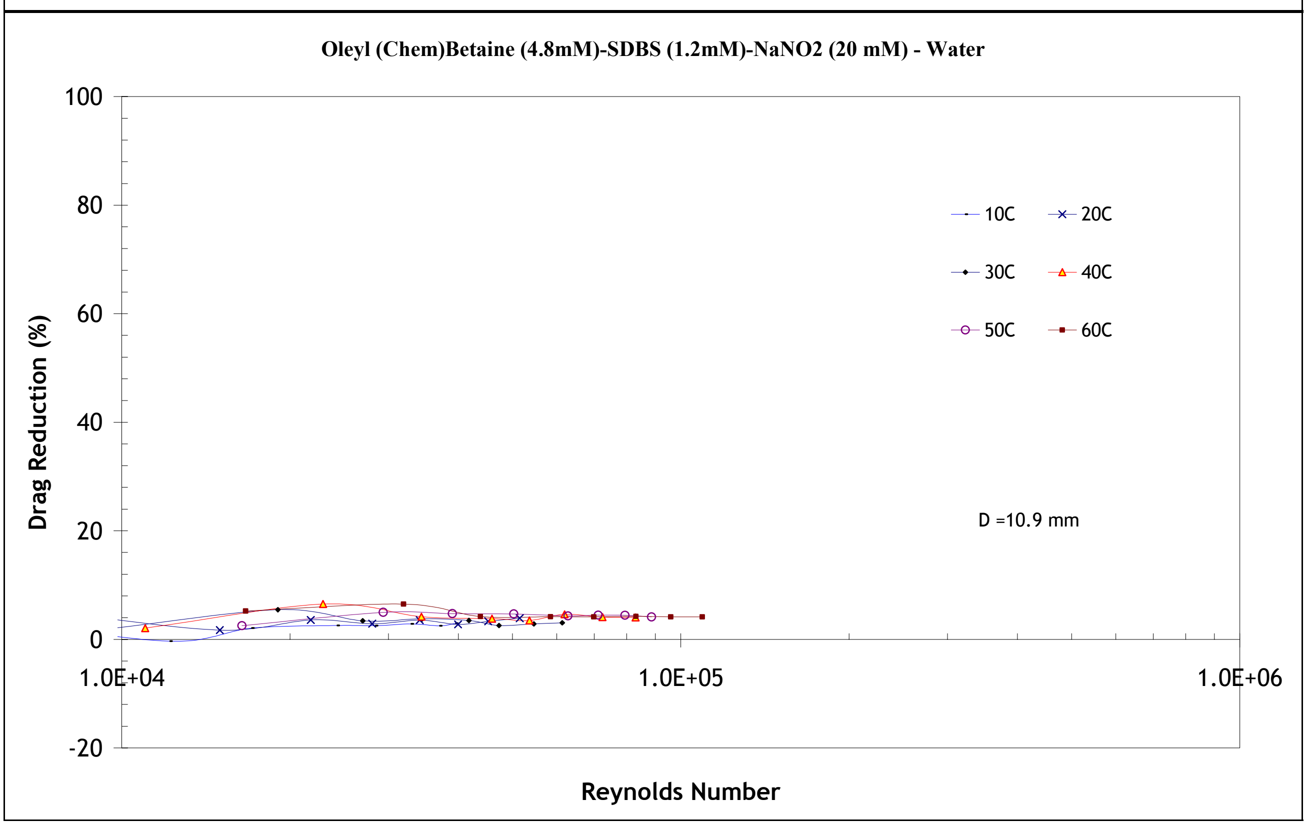

Oleyl Betaine(4.8mM)/SDS(1.2mM)+NaNO2(30mM) in 20%EG/Water
Drag Reduction (%)
Reynolds Number
-4C
5C
20C
30C
50C
D =10.9 mm
100
80
60
40
20
0
-20
1.0E+03
1.0E+04
1.0E+05

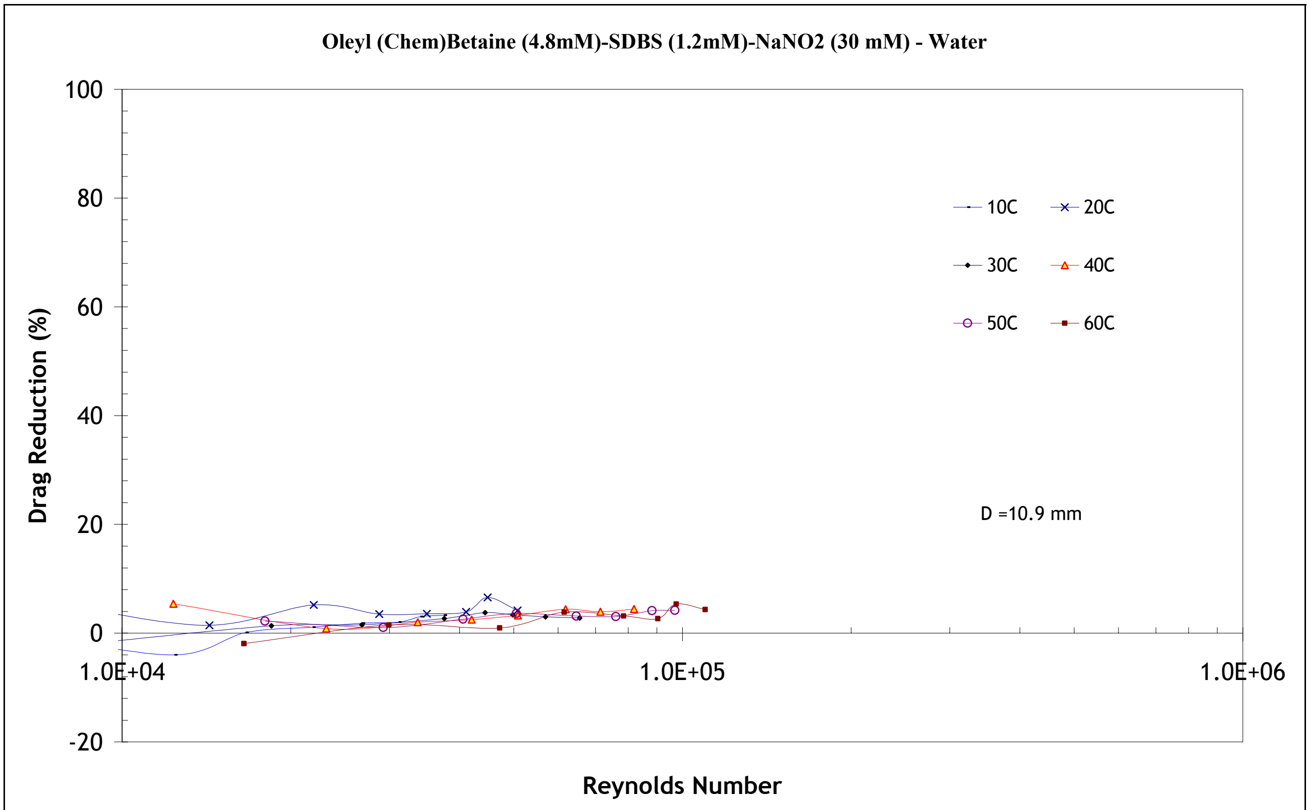
APPENDIX D

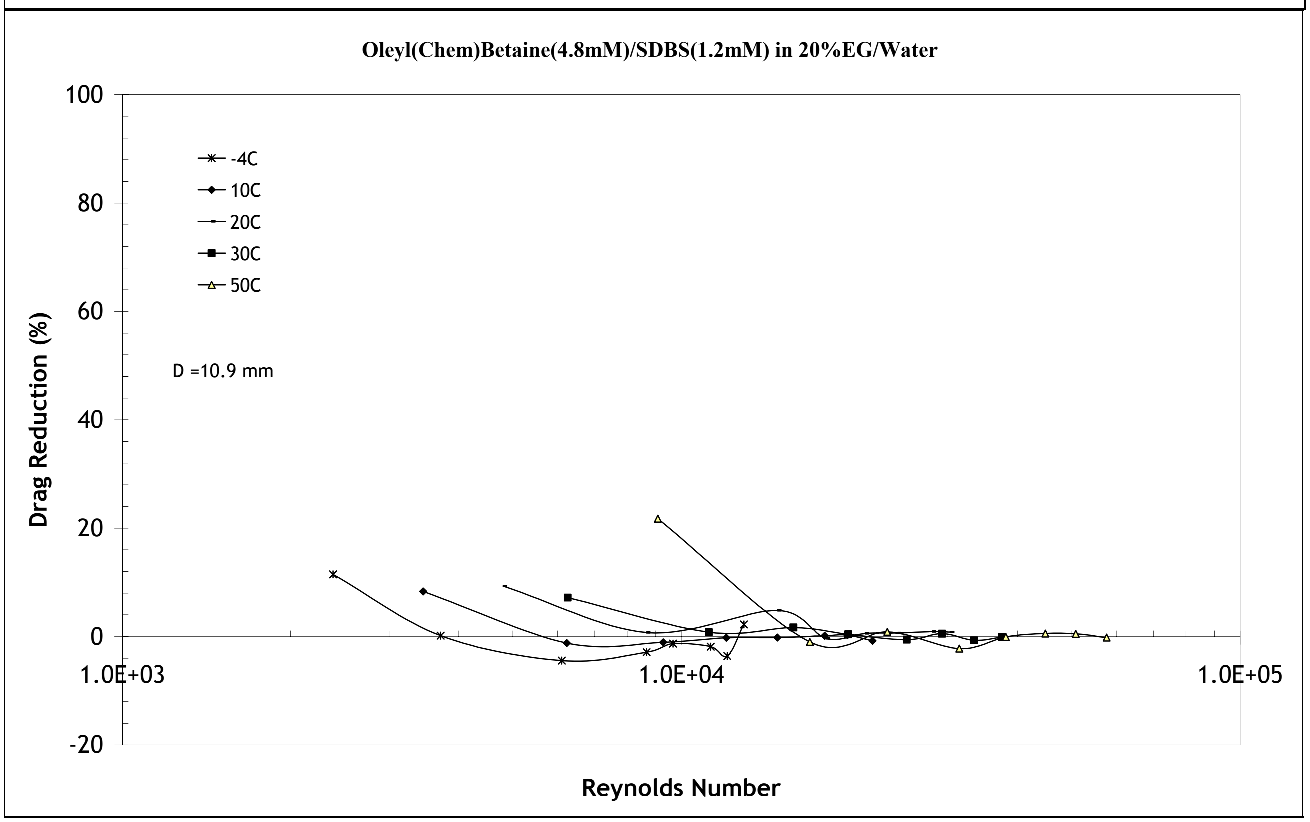

Oleyl (Chem)Betaine (4.8mM)-SDBS (1.2mM)-Water
Drag Reduction (%)
100
80
60
40
20
0
-20
1.0E+04
1.0E+05
1.0E+06
Reynolds Number
10C
20C
30C
40C
50C
60C
D =10.9 mm

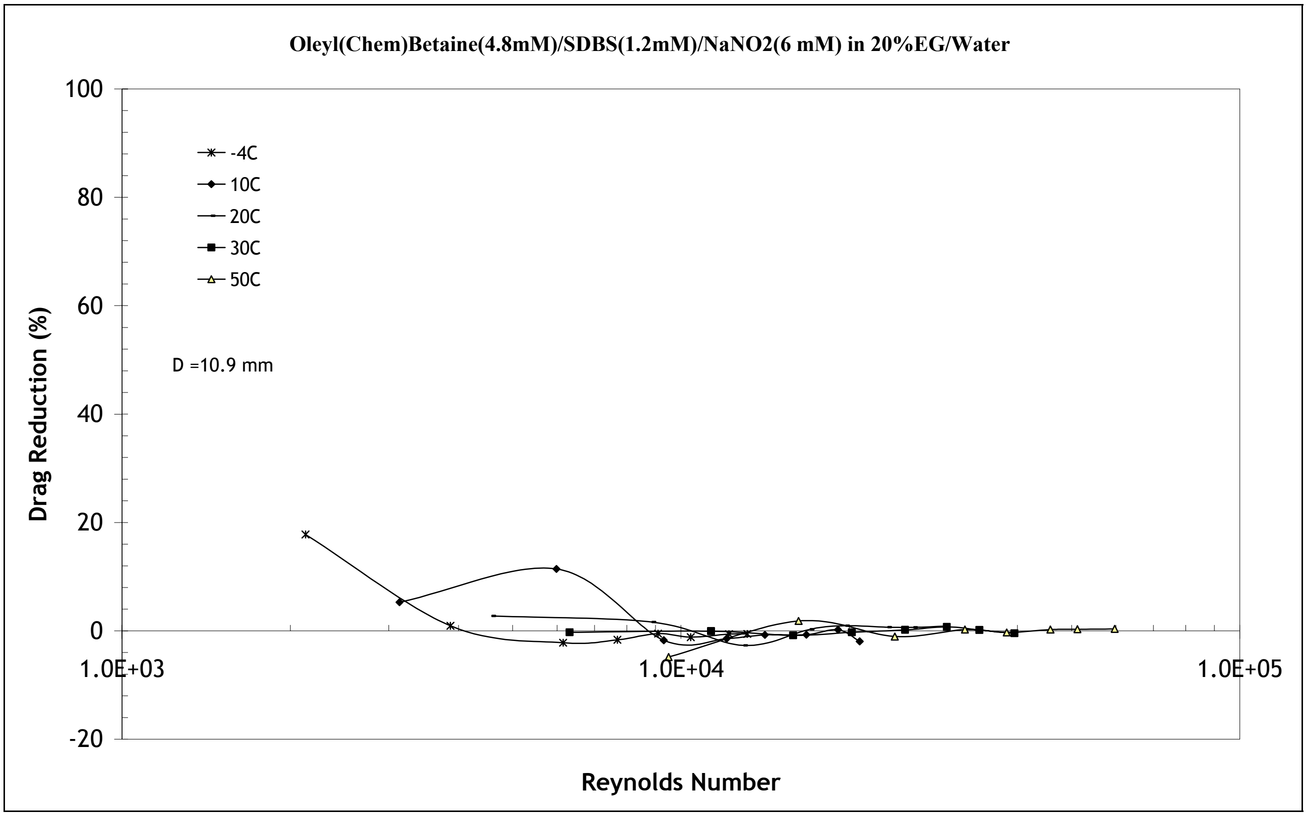

Oleyl (Chem)Betaine (4.8mM)-SDBS (1.2mM)-NaNO2 (6 mM) - Water
Drag Reduction (%)
100
80
60
40
20
0
-20
1.0E+04
1.0E+05
1.0E+06
Reynolds Number
10C
20C
30C
40C
50C
60C
D =10.9 mm


Oleyl (Chem)Betaine (4.8mM)-SDBS (1.2mM)-NaNO2 (12 mM) - Water
Drag Reduction (%)
100
80
60
40
20
0
-20
1.0E+04
1.0E+05
1.0E+06
Reynolds Number
10C
20C
30C
40C
50C
60C
D =10.9 mm

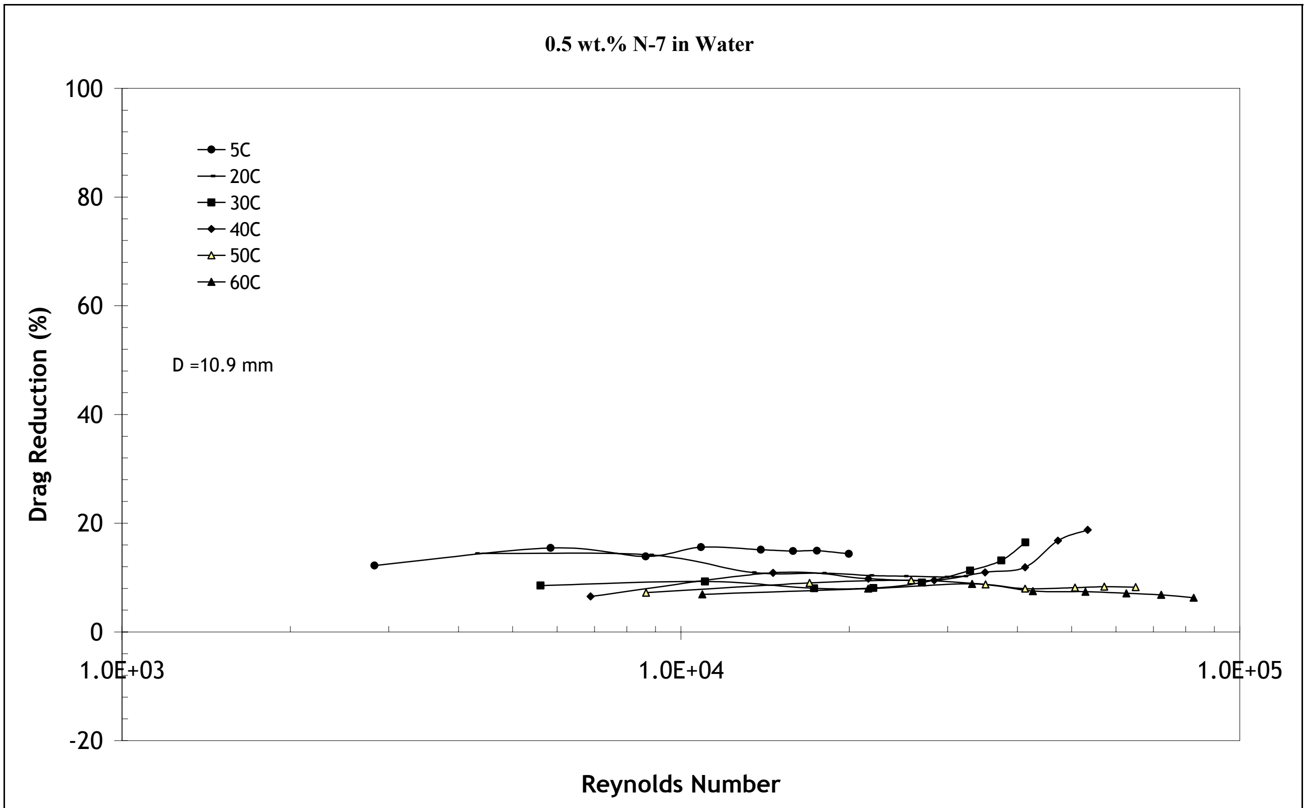

Oleyl (Chem)Betaine (4.8mM)-SDBS (1.2mM)-NaNO2 (20 mM) - Water
Drag Reduction (%)
100
80
60
40
20
0
-20
1.0E+04
1.0E+05
1.0E+06
Reynolds Number
10C
20C
30C
40C
50C
60C
D =10.9 mm

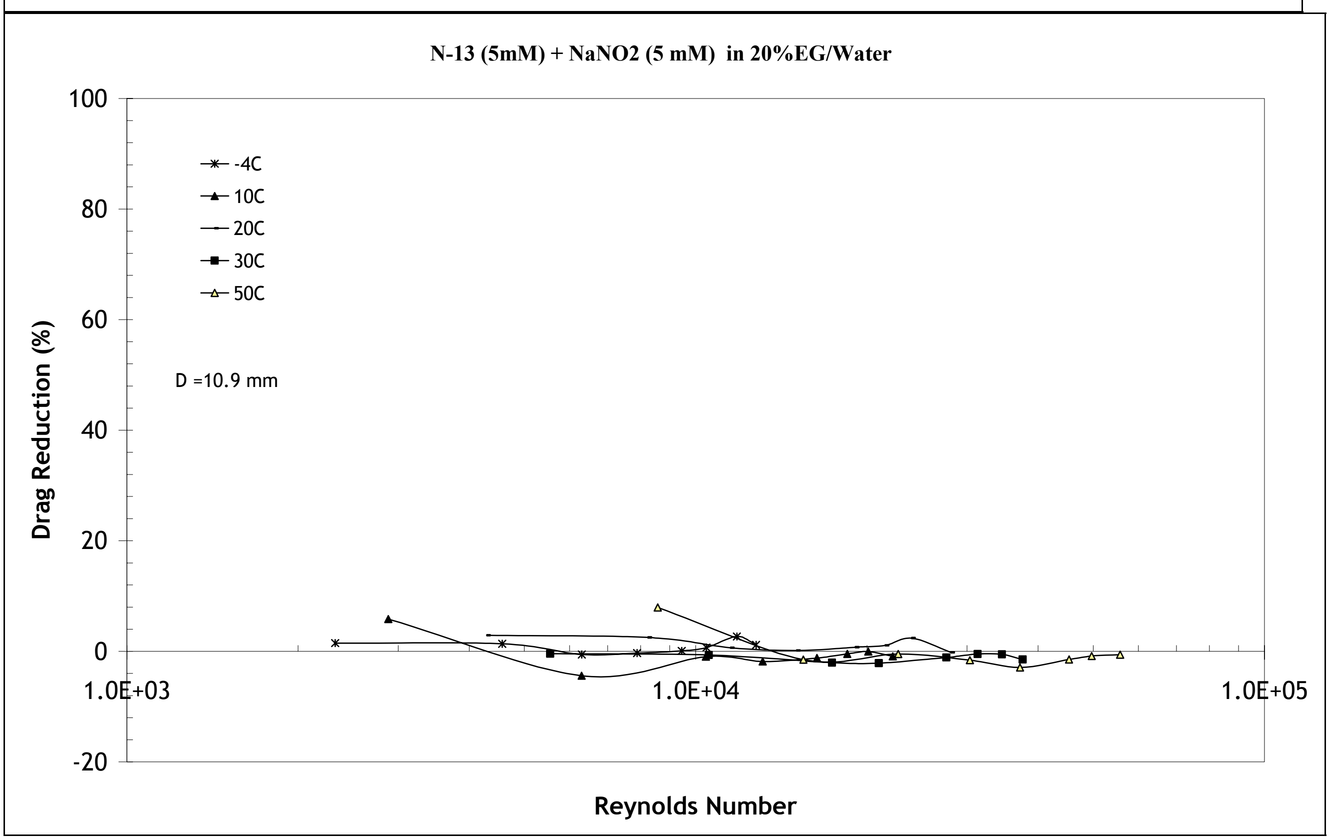

Oleyl (Chem)Betaine (4.8mM)-SDBS (1.2mM)-NaNO2 (30 mM) - Water
Drag Reduction (%)
Reynolds Number
10C
20C
30C
40C
50C
60C
D =10.9 mm
100
80
60
40
20
0
-20
1.0E+04
1.0E+05
1.0E+06

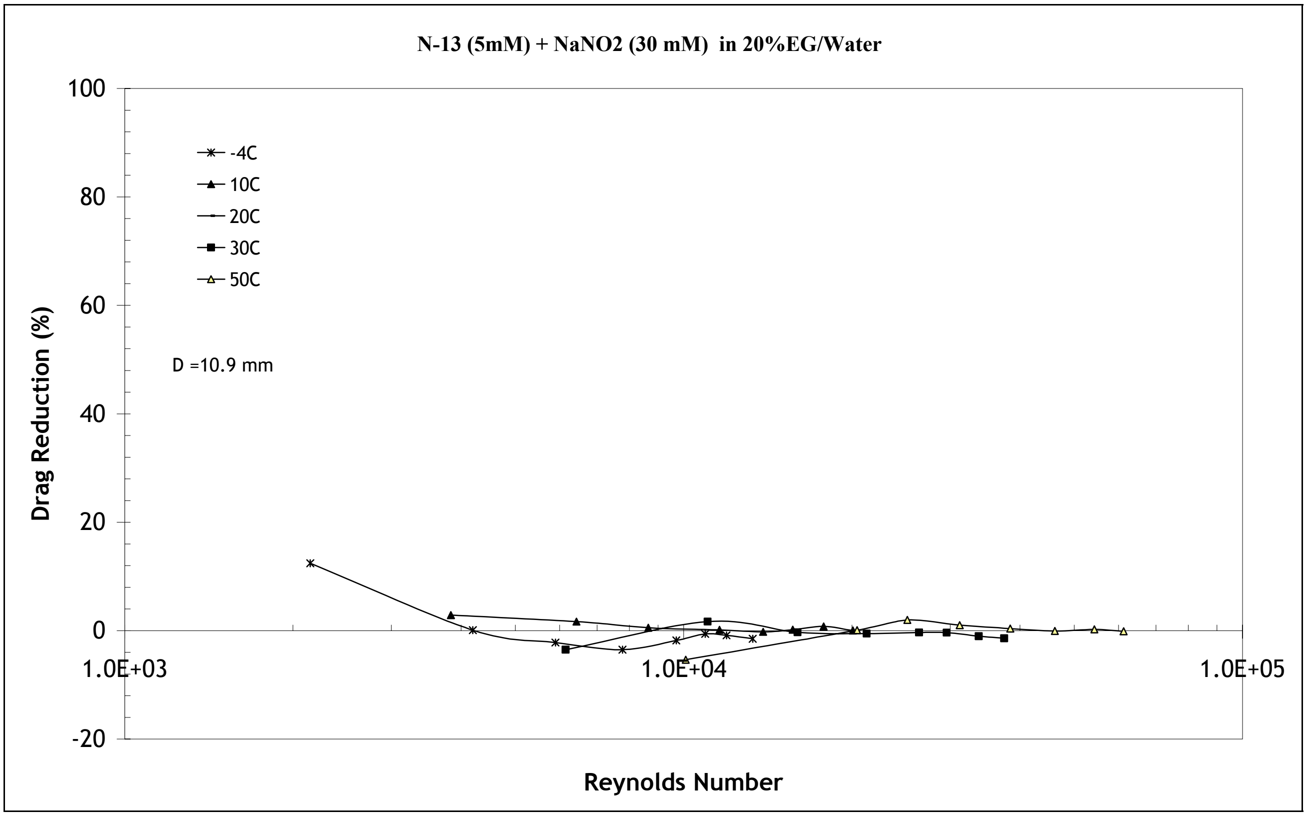

Oleyl(Chem)Betaine(4.8mM)/SDBS(1.2mM) in 20%EG/Water
Drag Reduction (%)
Reynolds Number
-4C
10C
20C
30C
50C
D =10.9 mm
100
80
60
40
20
0
-20
1.0E+03
1.0E+04
1.0E+05


Oleyl(Chem)Betaine(4.8mM)/SDBS(1.2mM)/NaNO2(6 mM) in 20%EG/Water
Drag Reduction (%)
Reynolds Number
-4C
10C
20C
30C
50C
D =10.9 mm
100
80
60
40
20
0
-20
1.0E+03
1.0E+04
1.0E+05

APPENDIX E


0.5 wt.% N-7 in Water
5C
20C
30C
40C
50C
60C
D =10.9 mm
Drag Reduction (%)
Reynolds Number
100
80
60
40
20
0
-20
1.0E+03
1.0E+04
1.0E+05


N-13 (5mM) + NaNO2 (5 mM) in 20%EG/Water
-4C
10C
20C
30C
50C
D =10.9 mm
Drag Reduction (%)
Reynolds Number
100
80
60
40
20
0
-20
1.0E+03
1.0E+04
1.0E+05



N-13 (5mM) + NaNO2 (30 mM) in 20%EG/Water
100
80
60
40
20
0
-20
Drag Reduction (%)
-4C
10C
20C
30C
50C
D =10.9 mm
1.0E+03
1.0E+04
1.0E+05
Reynolds Number